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Estudio termodinámico y cinético de los cambios de fase por Dinámica

Molecular Thermodynamic and kinetic study of phase changes by Molecular Dynamics

MEMORIA PARA OPTAR AL GRADO DE DOCTOR

PRESENTADA POR

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Memoria para optar
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Chapter 3

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Chapter 5

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Chapter 1

Resumen

Introducción

El fenómeno de la nucleación (formación de la fase más estable termodinámicamente a partir de una fase metaestable) es relevante en varios campos de la ciencia y la tecnología. Por ejemplo, la formación de hielo tiene influencia en el cambio climático [1, 2], en la criopreservación [3, 4] y en el procesamiento de alimentos [5]. La cristalización también es importante para la industria farmacéutica, pues afecta al diseño y producción de fármacos, ya que es la cinética y no la termodinámica la que pudiera controlar el polimorfismo del cristal obtenido [6]. La industria petrolera también se ve afectada por la nucleación, debido a la formación de clatratos de hidrocarburos en tuberías [7]. No solo resulta interesante el estudio de la transición líquido-sólido, pues el caso de la transición líquido-gas, la cavitación (formación de burbujas) también tiene mucho interés, por ejemplo en el diseño de procesos de destilación o de hélices de vehículos acuáticos, para evitar pérdida de rendimiento, excesivo ruido o daño en los componentes, [8, 9, 10] y también en geología debido al vulcanismo [11, 9], la erosión, la sonoquímica [12], la cavitación acústica [10] o la ebullición explosiva [8].

En los últimos años, se han utilizado métodos de simulación para estudiar la cinética de la formación de cristales y burbujas debido a las dificultades de estudiar estos eventos por medios experimentales. Las simulaciones moleculares permiten ver en detalle la representación de cómo comienza la nucleación cristalina o la cavitación. Esto es así porque frente a los experimentos o la teoría, las simulaciones tienen acceso a la escala relevante en estos procesos que es la nanoescala tanto en espacio como tiempo. Además las simulaciones nos permiten alcanzar condiciones que son complicadas de alcanzar experimentalmente, aunque a veces se requiere del uso de técnicas especiales de eventos raros como ya describiremos más adelante. En este trabajo, se estudian los cambios de fase partiendo de un líquido y utilizando la Dinámica Molecular, que permite el estudio del comportamiento del sistema formado por partículas, así como el cálculo de sus propiedades dinámicas y termodinámicas.

El primer paso para estudiar la cristalización o formación de burbujas con simulaciones es conocer el comportamiento de fase del sistema de interés. Aunque los diagramas de fase para sistemas puros se han estudiado ampliamente utilizan-

do Dinámica Molecular, aún no se conoce bien la metodología para estudiar la estabilidad termodinámica de las mezclas binarias, que son más relevantes y más abundantes que las sustancias puras. Por lo tanto, empezamos la tesis estableciendo una metodología eficiente para estudiar la estabilidad termodinámica de las mezclas binarias y obtener su diagrama de fase, lo que es un requisito previo para estudiar la nucleación o cavitación. Para ello partimos de la técnica conocida como Coexistencia Directa, que consiste en poner en contacto las fases entre las cuales se quiere determinar el punto de coexistencia.

El segundo paso fue el estudio de la nucleación y cavitación implementando y extendiendo la técnica conocida con el nombre de *Seeding* [13]. Esta técnica consiste en insertar una semilla de la fase emergente (estable) en el seno de la fase madre (metaestable) y surge en el contexto de la necesidad de usar técnicas especiales para estudiar estos eventos raros, dado que el tiempo que se requiere para estudiar el cambio de fase en un sistema con un volumen asequible para la simulación, puede ser demasiado elevado. Cuando surgió este método, ya existían otros más rigurosos, pero que tenían un elevado coste computacional y eran más complicados de aplicar. Por ello se encontró la necesidad de implementar un método que permitiese hacer un estudio de forma sencilla y más rápida para obtener una buena estimación de los parámetros que describen la nucleación. En esta tesis se ha ayudado a aclarar el uso de esta metodología y se ha extendido a nuevos sistemas.

Objetivos

Los principales objetivos de esta tesis se enumeran a continuación junto con el capítulo de resultados en el que se resuelven:

- Capítulo 5. Establecer una metodología clara para la aplicación del método de Coexistencia Directa en mezclas. Calcular el diagrama de fases para el sistema agua-NaCl, ya que el cloruro sódico es la sal más abundante en disolución acuosa, y es conveniente conocer la termodinámica de este sistema para un modelo que permita posteriormente el cálculo de la cinética de los cambios de fase.
- Capítulo 6. Entender cómo tener en cuenta el descenso crioscópico y por qué esto es importante, a la hora de desarrollar un nuevo modelo para sales en disolución acuosa. Comprobar si el modelo Madrid-2019 [14] es un buen potencial para reproducir esta curva de coexistencia entre hielo y disolución salina.
- Capítulo 7. Se ha visto que el punto débil del *Seeding* es la elección de un parámetro de orden, que nos permita distinguir entre partículas pertenecientes al sólido y al líquido para monitorizar el tamaño del clúster. Dependiendo del criterio elegido la tasa de nucleación [15] puede cambiar en

varios órdenes de magnitud. El objetivo es demostrar que usando un criterio adecuado para elegir el parámetro de orden se pueden obtener estimaciones correctas de las tasas de nucleación para el problema de la nucleación de sales iónicas en agua (NaCl en nuestro caso).

- Capítulo 8. Aplicar por primera vez la técnica *Seeding NVT* [16] para una transición líquido-gas de un sistema real de gran importancia, como es el agua. Predecir la línea de cavitación del agua con simulación y aclarar discrepancias existentes entre distintas medidas experimentales.
- Capítulo 9. Implementar por primera vez la técnica *Seeding NVT* para una transición líquido-gas de un sistema binario sencillo, estableciendo un método claro para que en un futuro se puedan estudiar otras mezclas más complejas.

Resultados

Siguiendo también la clasificación por capítulos que componen la parte de resultados, se van a enumerar los resultados más relevantes obtenidos en la tesis:

- Capítulo 5. Obtención del diagrama de fases agua-NaCl para el modelo JC-TIP4P/2005 [17, 18] por Coexistencia Directa. Este diagrama predice correctamente la coexistencia entre la disolución y el hielo, aunque subestima la solubilidad del NaCl. Conviene destacar que por primera vez se ha estudiado la coexistencia hidrohálita-disolución salina por simulación, los resultados obtenidos coinciden con una extrapolación lineal de los experimentos a altas temperaturas, a temperaturas más bajas parece que la curva experimental será subestimada, pero no se pudo estudiar la coexistencia donde hay experimentos debido a la cinética lenta del sistema. Esto sugiere que las interacciones ion-ion son demasiado fuertes en el modelo [19]. Este trabajo es un buen comienzo para el estudio de la cinética de nucleación en el sistema, y también para la mejora del modelo.
- Capítulo 6. Se demuestra que el modelo Madrid-2019 [14] reproduce el descenso crioscópico experimental de forma razonable para todas las sales estudiadas. Aunque observamos que la actividad del agua a lo largo de la curva de congelación no se reproduce bien (para reproducirla bien es necesario una entalpía y temperatura de fusión correctas). Por ello deducimos que al desarrollar un modelo para electrolitos, lo mejor es intentar reproducir la curva de coexistencia restando el error introducido por el uso de un modelo de agua que no reproduce correctamente la actividad. En nuestro caso el modelo proporciona buenos resultados por cancelación de errores entre el coeficiente osmótico de la sal y la actividad del agua [20]. Para

desarrollar modelos de sales sería una buena práctica tener en cuenta el descenso crioscópico, porque es fácil de determinar y da información sobre el coeficiente osmótico de disoluciones de electrolitos.

- Capítulo 7. Se demuestra que el criterio de *Mislabelling* es útil para seleccionar un parámetro de orden adecuado que permita distinguir entre partículas líquidas y sólidas, y obtener buenos resultados usando el *Seeding* [13] para el sistema estudiado (disolución acuosa supersaturada de NaCl). Las tasas de nucleación obtenidas en este trabajo, para la nucleación de NaCl a partir de una disolución supersaturada, son consistentes con métodos rigurosos como Foward Flux Sampling [21] o cristalización espontánea [22]. Esto sugiere que el *Seeding* en combinación con *Mislabelling* puede ser una herramienta extraordinariamente útil para estudiar la nucleación incluso en medios complejos como disoluciones iónicas [23].
- Capítulo 8. Por primera vez se aplica la técnica de *Seeding* al estudio de la cavitación de un sistema de interés experimental, el agua. Los resultados obtenidos son congruentes con experimentos de calentamiento isobárico [24] y enfriamiento isocórico en inclusiones de cuarzo [25, 26], así como con predicciones teóricas [27, 28]. Hay discrepancias con otras técnicas experimentales [29, 30, 31, 32, 33, 34, 35], pero creemos que podría deberse a que en estos experimentos se produzca nucleación heterogénea. Observamos que la energía libre interfacial disminuye al aumentar la curvatura de las burbujas, y da lugar a una longitud de Tolman de 0,1 nm. En general, este estudio proporciona una forma eficiente de investigar y comprender los factores que controlan y afectan la cavitación de agua, y de obtener información experimentalmente relevante a través de simulaciones [22].
- Capítulo 9. Se estableció la técnica *Seeding NVT* para su uso en mezclas binarias. Al estudiar la mezcla del modelo Lennard-Jones, se observa que la burbuja crítica es más pequeña en una mezcla binaria [22] que en el sistema puro a la misma presión de sobreestiramiento [16, 36]. Esto se explica porque la energía libre interfacial es aproximadamente un 25 % menor en la mezcla, lo que significa que el costo de energía libre de crear una burbuja es menor. La barrera de energía libre de la cavitación en el sistema puro y el de mezclas se fusiona en una sola curva cuando se representa como una función de la metaestabilidad escalada del líquido, indicando que el costo de crear una burbuja es similar en ambos [37].

Conclusiones

El principal objetivo de la tesis ha sido el estudio de transiciones de fase en sistemas moleculares desde un punto de vista termodinámico y cinético. Se empezó estudiando el equilibrio líquido-sólido y posteriormente estudiamos la nucleación

de cristales. Esto nos ha permitido poner a prueba campos de fuerza para la simulación de disoluciones acuosas de iones:

- Calculamos por primera vez el diagrama de fases completo del sistema agua-NaCl, concluyendo que las interacciones ion-ion del modelo JC-TIP4P/2005 son demasiado fuertes.
- Estudiamos la precipitación de NaCl en disoluciones acuosas saturadas, confirmando la tendencia a la agregación iónica en disoluciones supersaturadas. Además, se ha extendido la metodología de *Seeding* a este problema de manera exitosa gracias a la elección juiciosa de un parámetro de orden que proporciona resultados consistentes con técnicas de simulación más costosas. Este trabajo allana el camino de futuros estudios por simulación de precipitación.
- Examinamos el descenso crioscópico de varias sales y de esta forma validamos un nuevo modelo para disoluciones de electrolitos basado en la idea pionera de reescalar las cargas de las especies iónicas para emular la transferencia de carga.

A continuación se trató la transición líquido-vapor, concretamente la formación de burbujas en un líquido (cavitación):

- Obtuvimos por primera vez la línea de cavitación homogénea del agua mediante simulación lo cual nos ha permitido comparar de manera directa con resultados experimentales. El acuerdo con la teoría y con algunas técnicas experimentales para el estudio de la cavitación es muy bueno. Sin embargo, la discrepancia observada con otras técnicas sugiere que se está produciendo cavitación heterogénea en dichos experimentos.
- Observamos que la energía libre interfacial es menor en la mezcla que en el equivalente sistema puro, por tanto la burbuja crítica en una mezcla es más pequeña que en la sustancia pura. Además el coste energético de formar la burbuja es similar en ambos sistemas si la metaestabilidad del líquido es parecida.

1. Resumen

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Chapter 2

Summary

Introduction

The phenomenon of nucleation (formation of the thermodynamically most stable phase from a metastable phase) is relevant in various fields of science and technology. For example, ice formation influences climate change [1, 2], cryopreservation [3, 4], and food processing [5]. Crystallization is also important in the pharmaceutical industry as it affects the design and production of drugs, where the kinetics rather than thermodynamics may control the polymorphism of the obtained crystal [6]. The petroleum industry is also affected by nucleation due to the formation of hydrocarbon clathrates in pipelines [7].

Not only the study of the liquid-solid transition is interesting, but also the liquid-gas transition, as cavitation (formation of bubbles) is of great interest. For example, in the design of distillation processes or watercraft propellers, to avoid loss of performance, excessive noise, or damage to components [8, 9, 10], and also in geology due to volcanism [11, 9], erosion, sonochemistry [12], acoustic cavitation [10], or explosive boiling [8].

In recent years, simulation methods have been used to study the kinetics of crystal and bubble formation due to the difficulties of studying these events experimentally. Molecular simulations allow a detailed representation of the nucleation processes, as they have access to the relevant nanoscale in both space and time, which is not easily achievable experimentally. Additionally, simulations allow us to reach conditions that are difficult to achieve experimentally, although sometimes the use of special rare events techniques is required, as will be described later. In this work, phase changes starting from a liquid state are studied using Molecular Dynamics, which allows for the study of the behavior of the particle system, as well as the calculation of its dynamic and thermodynamic properties.

The first step in studying crystallization or bubble formation with simulations is to understand the phase behavior of the system of interest. While phase diagrams for pure systems have been extensively studied using Molecular Dynamics, the methodology for studying the thermodynamic stability of binary mixtures, which are more relevant and abundant than pure substances, is not yet well known. Therefore, we started the thesis by establishing an efficient methodology to study the thermodynamic stability of binary mixtures and obtain their phase diagram,

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which is a prerequisite for studying nucleation or cavitation. To do this, we used the technique known as Direct Coexistence, which involves bringing the phases between which the coexistence point is to be determined into contact.

The second step was the study of nucleation and cavitation by implementing and extending the technique known as Seeding [13]. This technique involves inserting a seed of the emerging (stable) phase into the bulk of the parent (metastable) phase and arose in the context of the need to use special techniques to study these rare events, as the time required to study the phase change in a system with a reasonable simulation volume can be too high. When this method emerged, there were already other more rigorous methods, but they were computationally expensive and more complicated to apply. Therefore, there was a need to implement a method that allowed for a simple and faster study to obtain a good estimation of the parameters that describe nucleation. This thesis has helped clarify the use of this methodology and has extended it to new systems.

Aims

The main objectives of this thesis are listed below along with the results chapter in which they are addressed:

- Chapter 5. Establish a clear methodology for the application of the Direct Coexistence method in mixtures. Calculate the phase diagram for the water-NaCl system, as sodium chloride is the most abundant salt in aqueous solution, and it is convenient to know the thermodynamics of this system for a model that allows the calculation of the kinetics of phase changes.
- Chapter 6. Understand how to take into account the freezing point depression and why this is important when developing a new model for salts in aqueous solution. Verify if the Madrid-2019 model [14] is a good potential to reproduce this coexistence curve between ice and saline solution.
- Chapter 7. It has been observed that the weak point of Seeding is the choice of an order parameter, which allows us to distinguish between particles belonging to the solid and the liquid in order to monitor the cluster size. Depending on the chosen criterion, the nucleation rate [15] can change by several orders of magnitude. The objective is to demonstrate that by using an appropriate criterion to choose the order parameter, correct estimates of the nucleation rates can be obtained for the problem of nucleation of ionic salts in water (NaCl in our case).
- Chapter 8. Apply for the first time the *Seeding NVT* technique [16] to a liquid-gas transition of a real system of great importance, such as water. Predict the cavitation line of water with simulation and clarify discrepancies existing between different experimental measurements.

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- Chapter 9. Implement for the first time the *Seeding NVT* technique for a liquid-gas transition of a simple binary system, establishing a clear method for studying more complex mixtures in the future.

Results

Following the chapter classification of the results section, the most relevant results obtained in the thesis are enumerated:

- Chapter 5. Obtaining the water-NaCl phase diagram for the JC-TIP4P/2005 model [17, 18] by Direct Coexistence. This diagram accurately predicts the coexistence between the solution and the ice, although it underestimates the solubility of NaCl. It is worth noting that, for the first time, the hydrohalite-salt solution coexistence has been studied by simulation, and the obtained results agree with a linear extrapolation of experiments at high temperatures. At lower temperatures, it seems that the experimental curve will be underestimated, but the coexistence could not be studied where experiments are available due to the slow kinetics of the system. This suggests that the ion-ion interactions are too strong in the model [19]. This work is a good starting point for the study of nucleation kinetics in the system, as well as for the improvement of the model.
- Chapter 6. It is demonstrated that the Madrid-2019 model [14] reasonably reproduces the experimental freezing point depression for all the studied salts. However, it is observed that the water activity along the freezing curve is not well reproduced (accurate reproduction would require correct enthalpy and melting temperature). Therefore, it is inferred that when developing a model for electrolytes, it is best to try to reproduce the coexistence curve while subtracting the error introduced by using a water model that does not correctly reproduce the activity. In our case, the model provides good results through error cancellation between the osmotic coefficient of the salt and the water activity [20]. To develop models for salts, it is recommended to consider freezing point depression as it is easy to determine and provides information about the osmotic coefficient of electrolyte solutions.
- Chapter 7. It is demonstrated that the Mislabelling criterion is useful for selecting an appropriate order parameter that allows distinguishing between liquid and solid particles, and obtaining good results using Seeding [13] for the studied system (supersaturated aqueous NaCl solution). The nucleation rates obtained in this work for NaCl nucleation from a supersaturated solution are consistent with rigorous methods such as Forward Flux Sampling [21] or spontaneous crystallization [22]. This suggests that Seeding in combination with Mislabelling can be an extraordinarily useful tool for studying nucleation even in complex media such as ionic solutions [23].

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- Chapter 8. For the first time, the Seeding technique is applied to the study of cavitation in an experimentally relevant system, water. The obtained results are consistent with isobaric heating experiments [24] and isochoric cooling in quartz inclusions [25, 26], as well as with theoretical predictions [27, 28]. There are discrepancies with other experimental techniques [29, 30, 31, 32, 33, 34, 35], but it is believed that they could be due to the occurrence of heterogeneous nucleation in these experiments. It is observed that the interfacial free energy decreases as the curvature of the bubbles increases, giving rise to a Tolman length of 0.1 nm. Overall, this study provides an efficient way to investigate and understand the factors that control and affect water cavitation, as well as to obtain experimentally relevant information through simulations [22].
- Chapter 9. The Seeding NVT technique was established for use in binary mixtures. When studying the Lennard-Jones model mixture, it is observed that the critical bubble is smaller in a binary mixture [22] than in the pure system at the same overstretching pressure [16, 36]. This is explained by the interfacial free energy being approximately 25% lower in the mixture, meaning that the free energy cost of creating a bubble is lower. The barrier of free energy for cavitation in the pure system and in mixtures merge into a single curve when represented as a function of the scaled metastability of the liquid, indicating that the cost of creating a bubble is similar in both [37].

Conclusions

The main aim of this thesis has been the study of phase transitions in molecular systems from a thermodynamic and kinetic point of view. We started by studying the liquid-solid equilibrium and later investigated crystal nucleation. This allowed us to test force fields for the simulation of aqueous ion solutions:

- We calculated, for the first time, the complete phase diagram of the water-NaCl system, concluding that the ion-ion interactions of the JC-TIP4P/2005 model are too strong.
- We studied the precipitation of NaCl in saturated aqueous solutions, confirming the tendency for ionic aggregation in supersaturated solutions. Additionally, we successfully extended the Seeding methodology to this problem by judiciously choosing an order parameter that provides consistent results with more computationally expensive simulation techniques. This work paves the way for future simulation studies of precipitation.
- We examined the freezing point depression of various salts and thus validated a new model for electrolyte solutions based on the pioneering idea of rescaling the charges of the ionic species to emulate charge transfer.

Next, we addressed the liquid-vapor transition, specifically the formation of bubbles in a liquid (cavitation):

- We obtained, for the first time, the homogeneous cavitation line of water through simulation, allowing us to directly compare with experimental results. The agreement with theory and some experimental techniques for studying cavitation is very good. However, the observed discrepancy with other techniques suggests that heterogeneous cavitation is occurring in those experiments.
- We observed that the interfacial free energy is lower in the mixture than in the equivalent pure system, therefore the critical bubble in a mixture is smaller than in the pure substance. Furthermore, the energy cost of forming the bubble is similar in both systems if the metastability of the liquid is similar.

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Capítulo 3

Discusión Integradora

Esta tesis profundiza en el conocimiento de los cambios de fase de la materia. Enfocamos el estudio desde dos disciplinas complementarias y fundamentales en este ámbito, la termodinámica y la cinética. El estudio termodinámico de un sistema nos informa de cuál es la fase más favorable desde el punto de vista de la energía libre en unas determinadas condiciones, o cuál es la fase a la que el sistema evolucionará de forma espontánea. Simplificando, la termodinámica nos permite conocer si un sistema es más estable en forma gaseosa, líquida o sólida a una presión, temperatura y concentración dadas. En otras palabras, la termodinámica nos permite obtener un diagrama de fases del sistema de estudio. Por otro lado, la cinética en el contexto de los cambios de fase, estudia la velocidad con que se produce el proceso de transición de fase y los factores que afectan al mismo. El estudio cinético tiene gran importancia, ya que aunque una fase sea la más estable en unas determinadas condiciones termodinámicas, no significa que nos vayamos a encontrar el sistema en dicha fase, debido a que la cinética con la que el sistema evoluciona a la fase más estable puede ser lenta. Poniendo un ejemplo cotidiano, la forma más estable del carbono en las condiciones que se presentan en la superficie terrestre es el grafito, pero también nos podemos encontrar diamantes, que son la fase estable a presiones mucho más altas que la atmosférica. Esto es así porque la transición de fase diamante-grafito es muy lenta. Como parece que el diamante fuera una fase estable termodinámicamente aun no siéndolo, se dice que el diamante es la forma metaestable, "falsamente estable". En esta tesis cuando hablamos del estudio cinético nos referimos al estudio de la nucleación, es decir la formación de la fase estable en el seno de la fase madre metaestable. Este proceso comienza con la formación de un núcleo (clúster, agregado) de la nueva fase. Hay un término que favorece la formación de este núcleo porque la nueva fase es más estable y otro que se opone porque se requiere energía libre para crear la nueva interfaz, de aquí surge la barrera de energía libre de formación del núcleo de la nueva fase. En ausencia de superficies o impurezas, la barrera de energía libre solo se supera por fluctuaciones térmicas, lo que hace que este proceso sea a veces un evento raro. El tamaño de clúster de la nueva fase que determina el fin de la nucleación y el comienzo del crecimiento se denomina crítico [1, 2]. Este estado corresponde a la parte superior de la barrera de energía libre que separa la fase madre y la nueva fase. Concretamente vamos a tratar el

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caso de la transición líquido-sólido o cristalización, refiriéndonos a la formación de un clúster de partículas sólidas, o núcleo, en el sistema líquido. Y el caso de la transición líquido-vapor, denominada habitualmente como cavitación, en este fenómeno surge una burbuja de gas en el seno del líquido.

Para llevar a cabo el estudio cinético de una transición de fase de forma efectiva, hay que conocer cuál es la fase estable en las condiciones de estudio (es decir hacia qué fase evolucionará el sistema), y cuál es el grado de metaestabilidad del sistema, o en otros términos, cómo de lejos estamos de las condiciones de coexistencia entre la fase inicial y final, y por tanto de las condiciones en las cuales sería estable la fase de la cual partimos. El grado de metaestabilidad del sistema determinará que técnicas podemos emplear para el estudio de la nucleación, se profundizará en esto a lo largo de la tesis. En el capítulo 4 se ahondará en qué es la nucleación y la teoría más extendida para explicarla, la Teoría Clásica de Nucleación (CNT) [3, 4, 5, 6], que como ya veremos hace ciertas aproximaciones, por lo que hay que evaluar su validez en cada caso de estudio.

Cabe destacar que se ha usado el paquete GROMACS [7], que produce simulaciones por ordenador de Dinámica Molecular, para llevar a cabo los estudios que componen esta Tesis. Elegimos esta herramienta porque tanto la teoría como los experimentos tienen una importante limitación y es que no tienen acceso a información detallada a escala molecular. Por ejemplo, en el evento de nucleación o cavitación, el núcleo crítico o la burbuja crítica (que tiene un 50 por ciento de posibilidades de crecer o disolverse) no puede visualizarse experimentalmente debido a su pequeño tamaño y corta vida. Además, el tamaño y la vida típicos de un núcleo crítico son nanoscópicos y no conocemos de antemano cuándo o dónde se va a producir [8]. Las simulaciones por ordenador pueden acceder a dicha información y han sido utilizadas extensamente para estudiar los cambios de fase.

La simulación molecular se ha convertido en una herramienta valiosa para estudiar la nucleación porque tiene acceso a la escala relevante [9, 10, 11]. Sin embargo, la disparidad de tiempo entre la vida del núcleo y la ocurrencia de la nucleación, sumado a que normalmente los experimentos se realizan en condiciones en las que las tasas de nucleación son demasiado bajas en comparación con los tiempos típicos de las simulaciones, hacen necesario usar métodos especiales de eventos raros. Por ello, a menudo se requieren técnicas de simulación especiales para eventos raros, como *Umbrella Sampling* [12, 13, 14, 15], *Forward-Flux Sampling* (FFS) [16, 17, 18, 19, 20], *Transition Path Sampling* [21, 22, 23, 24] o *Metadynamics* [25, 26, 27]. Aunque estos métodos son rigurosos, a menudo son técnicamente exigentes y requieren mucha capacidad de cálculo [28]. Como alternativa, en los últimos años el método *Seeding* ha ido ganando popularidad, principalmente debido a que es más fácil de implementar y más eficiente desde un punto de vista computacional [29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41]. Este método es el que usaremos en esta tesis cuando se requiera de una técnica

especial para estudiar la nucleación o cavitación. Consiste en insertar una semilla de la fase estable dentro del líquido metastable y buscar las condiciones para las cuales la semilla insertada es crítica, es decir, está en la cima de la barrera de energía libre que separa las fases metastable y estable.

Parece lógico pues, que antes de estudiar la cinética de un sistema hay que tratar su termodinámica. Por ello en esta tesis se empezó aprendiendo y desarrollando la metodología para estudiar la termodinámica. En particular, estudiamos el diagrama de fases del sistema NaCl-agua (capítulo 5) y el descenso crioscópico (línea que indica cuando es favorable la formación de hielo a partir de agua y viceversa) para distintas sales en agua, más específicamente para el cloruro sódico (NaCl), el cloruro potásico (KCl), el cloruro de litio (LiCl), el cloruro de magnesio (MgCl₂) y el sulfato de litio (Li₂SO₄) (capítulo 6). Estos trabajos dieron lugar a dos publicaciones en *The Journal of Chemical Physics* [42, 43]. A continuación se estudió la cinética de la formación de sal común sólida (NaCl) a partir de su disolución acuosa (capítulo 7), trabajo que fue publicado en la revista llamada *Physical Chemistry Chemical Physics* [39]. Los tres capítulos nombrados hasta ahora estudian cambios de fase líquido-sólido, pero no nos quedamos ahí, sino que estudiamos también la transición líquido-vapor, lo que se recoge en otras dos publicaciones en *The Journal of Chemical Physics* [40, 41]. En ambas, lo primero que se estudia es la termodinámica, para conocer la presión de coexistencia a la temperatura de trabajo, y luego la cinética mediante *Seeding NVT*. Esta técnica únicamente se había aplicado a sistemas puros sencillos con interacciones Lennard-Jones (LJ) para estudiar cavitación [35, 36, 37]. En esta tesis, por un lado introducimos la novedad de aplicarla a un sistema de gran interés como es el agua (capítulo 8), comparando los resultados satisfactoriamente con experimentos, y por otro lado publicamos la adaptación de la técnica a una mezcla sencilla con un modelo LJ estableciendo las bases de cómo aplicar la técnica a mezclas (capítulo 9).

Ahora, se va a explicar resumidamente en qué consisten las cinco publicaciones que acabamos de nombrar y que componen la parte de resultados de esta tesis, de manera que se presentará cuál fue su motivación y sus hallazgos más importantes.

El primer capítulo de resultados, capítulo 5, está dedicado al estudio del diagrama de fases del sistema agua-NaCl. Empezamos por aquí porque es donde se establece la metodología de la técnica de Coexistencia Directa aplicada a mezclas para conocer el diagrama de fases de un sistema multicomponente. Además, para entender el interés intrínseco de este sistema, hay que destacar que las disoluciones acuosas salinas son abundantes, las encontramos en un gran abanico que va desde el agua de mar hasta las disoluciones fisiológicas. La sal más abundante y por ello conocida como sal común, es el cloruro sódico (NaCl), siendo el comportamiento de fase de las mezclas de agua-NaCl de gran interés [44, 45]. Estas diso-

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luciones pueden cristalizar en hielo, NaCl o hidrohalita ($\text{NaCl} \cdot 2\text{H}_2\text{O}$) dependiendo de las condiciones de concentración y temperatura [46, 44, 47, 45, 48, 49, 50]. El estudio de los factores termodinámicos y cinéticos que controlan el tipo de fase o fases presentes es muy importante en ciencia atmosférica [44], geología [51, 52] y criopreservación [49, 50] entre otros.

Aunque el diagrama de fases termodinámico para las mezclas de agua y NaCl ya es conocido experimentalmente [53, 54, 55, 45], el estudio de la cinética de las transiciones de fase sigue siendo un gran desafío [56, 57, 46, 47, 58, 59, 45, 48]. Hemos mencionado que la simulación molecular es una herramienta muy adecuada para el estudio de la nucleación de cristales porque tiene acceso a la escala nanoscópica, que es la relevante para la comprensión del inicio de la cristalización [60, 9]. Esto requiere un conocimiento detallado del diagrama de fases de equilibrio, por eso en este trabajo calculamos el diagrama de fases para el sistema NaCl- H_2O para el modelo TIP4P/2005-JC [61, 62]. Por otro lado, antes de este trabajo nadie había intentado calcular la coexistencia entre la disolución acuosa de NaCl y la hidrohalita. Sin embargo, calcularlo no es fácil, han sido necesarios muchos años para llegar a un consenso en el cálculo de la solubilidad del NaCl para una sola temperatura [63, 64, 65, 66, 67, 68, 69, 70, 71, 72]. Por ello en este trabajo explicamos en detalle y comparamos dos procedimientos para aplicar la técnica de Coexistencia Directa para sistemas de mezclas, que consiste en simular las fases en contacto de las cuales se quiere conocer el punto de coexistencia. Más concretamente los métodos propuestos son:

- Método del acotado, que consiste en simular la disolución en contacto con la fase sólida (hielo, sal sólida o hidrohalita) manteniendo la concentración de la disolución constante mediante el uso de grandes sistemas y la realización de simulaciones de corta duración. Se determina si la fase sólida crece o funde en las simulaciones, para acotar así la temperatura (fijando la presión) a la cual las fases estarían en coexistencia (el hielo ni funde ni crece).
- Método del equilibrado, en el que se simula el sistema con ambas fases, a una presión y temperatura determinadas, el tiempo suficiente como para que se alcance el equilibrio y poder medir la concentración de coexistencia. Para un sistema de dos componentes, este enfoque es muy útil, ya que, según la regla de las fases de Gibbs, dos fases pueden estar en equilibrio para un valor impuesto de presión y temperatura.

Se ha comprobado que se obtienen resultados equivalentes con ambos métodos. Al final obtenemos un diagrama de fases que predice correctamente la coexistencia entre la disolución y el hielo. Para la coexistencia entre la disolución y la $\text{NaCl} \cdot 2\text{H}_2\text{O}$ no fue posible establecer una comparación directa con los resultados experimentales porque las simulaciones a las temperaturas y concentraciones en el rango de interés experimental eran demasiado lentas y solo se obtuvieron resultados concluyentes a temperaturas más altas. Además, se encontró que el modelo subestima la solubilidad del NaCl, lo que sugiere que las interacciones ion-ion

son demasiado fuertes en el modelo JC-TIP4P/2005. Este trabajo constituye un buen punto de partida para la mejora del modelo y el estudio de la cinética de nucleación. En general, el modelo JC-TIP4P/2005 proporciona una descripción razonable del diagrama de fases, pero se requiere trabajo adicional para desarrollar un modelo que prediga exactamente todas las curvas de coexistencia y otras propiedades termodinámicas y dinámicas.

Ya hemos explicado la importancia de las disoluciones acuosas salinas. Por lo tanto, la disponibilidad de un modelo de potencial capaz de reproducir el comportamiento termodinámico y dinámico de estas disoluciones sería de gran interés. Desafortunadamente, esto ha resultado ser un desafío y la mayoría de los potenciales existentes no logran reproducir gran parte de su comportamiento. En particular, la difusión del agua o la solubilidad de la sal a menudo no se reproducen bien (como demostramos en el anterior trabajo, capítulo 5). Recientemente se propuso el modelo Madrid-2019, que utiliza el modelo TIP4P/2005 para el agua y cargas parciales para los iones, y se ha demostrado que proporciona una buena descripción de numerosas propiedades, incluyendo densidades de disolución, viscosidades y difusión del agua. En este trabajo, evaluamos su fiabilidad en la evaluación del descenso crioscópico (curva de coexistencia entre disolución y hielo). Aunque esta propiedad es coligativa, es decir que a bajas concentraciones de electrolito depende únicamente de la concentración del electrolito sin importar su identidad química, se necesita un buen modelo de las sales para predecir con precisión el descenso crioscópico en concentraciones de moderadas a altas. Para calcular la curva de coexistencia entre el hielo y varias disoluciones acuosas de sal (NaCl, KCl, LiCl, MgCl₂ y Li₂SO₄), utilizamos simulaciones de Coexistencia Directa con la metodología explicada en el capítulo 5, concretamente se utiliza el método del equilibrado.

Nuestros resultados muestran que el modelo Madrid-2019 reproduce bastante bien el descenso crioscópico experimental para todas las sales y todas las composiciones consideradas (hasta el punto eutéctico). Los mejores resultados se obtienen para las sales de KCl y LiCl. Por otro lado para las disoluciones de NaCl, MgCl₂ y Li₂SO₄ se subestima ligeramente el descenso crioscópico. Al analizar las posibles causas de las diferencias entre los datos simulados y experimentales, descubrimos que el modelo de agua TIP4P/2005 introduce cierto error en la actividad del agua a lo largo de la curva de congelación. Por lo tanto, llegamos a la conclusión de que al desarrollar un modelo para electrolitos en vez de intentar reproducir la curva de fusión experimental, lo mejor es intentar reproducir la curva de coexistencia restando el error introducido por el uso de un modelo que no reproduce exactamente la actividad del agua. De lo contrario, el modelo de electrolito solo puede proporcionar una estimación precisa mediante la cancelación de errores entre la descripción de la actividad del agua y el coeficiente osmótico de la sal. Este es el caso del modelo Madrid-2019 para el NaCl, que subestima el coeficiente osmótico en todo el rango de concentraciones, pero a molalidades mayores que 1 mol kg⁻¹, las curvas simuladas y experimentales son paralelas en-

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tre sí. Esta subestimación del coeficiente osmótico compensa hasta cierto punto la mayor actividad del agua del modelo TIP4P/2005 para un sobreenfriamiento dado, produciendo curvas de coexistencia razonables. Se debe tener en cuenta que reproducir la curva sin cancelación de errores requeriría un modelo de agua con la temperatura y entalpía de fusión correctas y un campo de fuerza de iones capaz de reproducir el coeficiente osmótico hasta altas concentraciones para temperaturas muy por debajo de la temperatura de fusión del agua pura. Ciertamente, aún no se ha propuesto un campo de fuerza como ese. El modelo Madrid-2019 está lejos de ser perfecto, pero hace un trabajo razonable en describir los resultados experimentales. Esto se suma al número de propiedades cuya descripción mejora con el modelo Madrid-2019 en comparación con otros modelos no polarizables con cargas enteras, que incluyen las densidades, viscosidades y coeficientes de difusión de disoluciones salinas en condiciones atmosféricas hasta el propio límite de solubilidad [73], e incluso el límite de solubilidad de NaCl [74]. El compromiso es que los potenciales con cargas parciales no son adecuados para describir propiedades de sales puras [75, 76]. Con este trabajo esperamos que el descenso crioscópico se convierta en una propiedad estándar a tener en cuenta al desarrollar potenciales para electrolitos, ya que actualmente su determinación es relativamente sencilla. Además, proporciona información fácil y directa sobre el coeficiente osmótico de disoluciones de electrolitos, que se calcula inmediatamente a lo largo de la curva de coexistencia.

Tras haber descrito las técnicas necesarias para conocer el diagrama de fases o puntos de coexistencia en un sistema podemos pasar a estudiar los inicios de los cambios de fase, específicamente empezamos con la formación de un cristal en el seno de un líquido por nucleación.

Como ya mencionamos en esta tesis para estudiar la nucleación en condiciones en las que no se puede observar la cristalización de forma espontánea usamos la técnica *Seeding*. El *Seeding* aprovecha el hecho de que el núcleo crítico, bajo condiciones isobáricas-isotérmicas (NpT), es un estado de equilibrio inestable, que aparece en el máximo de la curva de energía libre de nucleación. Este clúster tiene un cincuenta por ciento de posibilidades de disolverse o crecer hacia la cristalización de todo el sistema. Por lo tanto, al insertar una semilla cristalina dentro de un líquido metaestable pre-equilibrado y luego seguir la evolución del tamaño de la semilla a lo largo de la simulación, se puede estimar el tamaño crítico en las condiciones estudiadas. Si combinamos este tamaño del clúster con otras propiedades de las fases líquida y cristalina *bulk* y la Teoría Clásica de Nucleación [3, 4, 5, 6] obtenemos valores aproximados de los parámetros más relevantes en el estudio de la nucleación: la tasa de nucleación, la altura de la barrera de energía libre de nucleación y la energía interfacial.

La parte más delicada del método de *Seeding* es la estimación del tamaño del núcleo crítico. Diferentes criterios para distinguir las partículas que pertenecen al sólido (o para determinar el radio de la burbuja en el caso del equilibrio líquido-vapor) pueden conducir a diferencias sustanciales en las estimaciones de

la tasa de nucleación, como se concluyó para la tasa de nucleación de NaCl a partir de una disolución supersaturada utilizando el modelo JC/SPC/E en la Ref. [77]. Esto parece un resultado desalentador para los usuarios actuales o potenciales del *Seeding* [78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95]. Por eso decidimos llevar a cabo el trabajo del capítulo 7, en el cual demostramos que usando el criterio de *Mislabelling* para elegir un parámetro de orden educado que distinga partículas pertenecientes al líquido o al sólido [34] se puede solucionar el problema presentado en la referencia [77]. Esta técnica consiste en que el número de partículas mal etiquetadas con el parámetro de orden sea igual para el líquido y sólido *bulk*.

El criterio de *Mislabelling* ha demostrado ser exitoso para esferas duras [34, 96, 97], Lennard-Jones [34], agua [33, 98, 99, 100, 101], NaCl [102], hielo desde una disolución salina [103, 104] y coloides de cargas opuestas [105]. Sin embargo, esto no garantiza el éxito para cualquier sistema y hay que probarlo para cada caso específico, que es precisamente lo que hacemos en este trabajo para la nucleación del NaCl a partir de su disolución acuosa supersaturada. Los resultados obtenidos muestran consistencia con métodos rigurosos y que no dependen del parámetro de orden como el FFS [20] o la cristalización espontánea, que también hemos estudiado en este capítulo. Así pues, este trabajo suma un sistema más en el que se han aplicado conjuntamente y con éxito el *Seeding* con el *Mislabelling* y respalda su uso para obtener estimaciones rápidas y razonablemente precisas de la tasa de nucleación. Además sugiere que, siempre que se implemente un buen parámetro de orden en el *Seeding*, este puede ser un enfoque muy poderoso para estudiar la nucleación incluso en medios complejos como son las disoluciones iónicas.

Tras haber estudiado la nucleación cristalina mediante *Seeding* nos adentramos en un terreno menos explorado, el de la formación de burbujas de vapor en un líquido metaestable, la cavitación. Este es un proceso activado, al igual que la nucleación, debido al costo de energía libre de crear una interfaz entre ambas fases. Dicha penalización energética permite la metaestabilidad, *i.e.* la existencia del líquido más allá de sus fronteras termodinámicas.

Establecer los límites de estabilidad de un líquido tan ubicuo como el agua tiene importantes implicaciones prácticas y, por lo tanto, ha atraído mucha atención. Diferentes estrategias experimentales y análisis teóricos se han utilizado para medir y predecir la línea de cavitación, o el límite de estabilidad cinética presión-temperatura del agua líquida. Determinar la ubicación de la línea de cavitación requiere conocer la dependencia de la tasa de cavitación con la presión y la temperatura.

Como mencionamos anteriormente, esto es difícil de obtener en experimentos y en simulación requiere del uso de métodos de simulación especiales. Si a esto le sumamos el hecho de que el agua es un sistema costoso desde un punto de vista computacional debido a la presencia de interacciones electrostáticas, es comprensible que el estudio de cavitación por simulación para el agua sea escaso. Menzl

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et al. son pioneros en este campo [106], usaron simulaciones con un sesgo que promovía la aparición de burbujas en el líquido sobreestirado, así fueron capaces de calcular la tasa de nucleación versus la presión del líquido para una temperatura de 296,4 K. Conociendo la tasa de nucleación, se puede estimar la presión a la que se producirá la cavitación en un determinado montaje experimental, lo que permite predecir la ubicación de la curva de cavitación. En este caso se reportó una presión de cavitación de -126 MPa a la temperatura estudiada para el modelo de agua TIP4P/2005 [61], lo que concuerda con las medidas experimentales.

En el trabajo del capítulo 8 estudiamos la cavitación del agua, con el modelo TIP4P/2005 [61]. El estudio se centra en dos temperaturas, 450 K y 550 K, lo que permite una comparación más directa con el régimen en el que están disponibles la mayoría de los puntos experimentales de la línea de cavitación homogénea. Para ello usamos una técnica que hasta el momento de la publicación de nuestro trabajo [40] se había aplicado únicamente a sistemas arquetipo sencillos del modelo Lennard-Jones [36, 37]. Esta técnica es una variante del *Seeding*, que acabamos de ver en el contexto del capítulo 7. La diferencia es que ahora lo aplicamos al caso de la cavitación, lo que supone seguir el tamaño de la burbuja de forma distinta a como se seguía el clúster sólido. Ahora seguimos el radio y no el número de partículas pertenecientes al clúster de la nueva fase. Por otro lado las ecuaciones empleadas se deducen en el capítulo 4 y veremos que tampoco coinciden exactamente debido a la validez o no de ciertas aproximaciones utilizadas. Además, en vez de llevar a cabo las simulaciones en el colectivo NpT las desarrollamos en el colectivo canónico (NVT). Este colectivo presenta la ventaja frente al NpT de que la burbuja se mantiene estable en el tiempo, pues coincide con el mínimo de energía de Helmholtz (en el NpT vimos que coincidía con el máximo en energía de Gibbs), lo que nos permite tener más estadística sobre el tamaño de la burbuja y su naturaleza, aparte de que se necesita una única simulación por cada punto de coexistencia [36, 107].

Antes de comenzar las simulaciones para el estudio de la cavitación como ya sabemos, debemos conocer la presión de coexistencia (líquido-gas) a la temperatura a la que trabajamos. Por ello lo primero que se hizo fue hacer este cálculo mediante el método de Coexistencia Directa en el NVT para obtener los componentes de presión del sistema en equilibrio. Obtuvimos un valor de 4,49 bar para la temperatura de 450 K que está en concordancia con el de las referencias [108, 109] y una energía interfacial (usando la ruta mecánica [110]) de (40 ± 1) mJ m $^{-2}$ también en concordancia con la literatura [109]. Para la temperatura de 550 K obtenemos una presión de vapor de (39 ± 1) bar y una energía interfacial de (17 ± 2) mJ m $^{-2}$, también en concordancia con las referencias [108, 109].

Una vez conocidos los puntos de coexistencia se procede a estudiar la cavitación, al sobreestirar profundamente (es decir someter a altas tensiones o presiones negativas) el agua líquida por debajo de la presión de coexistencia, somos capaces de observar y cuantificar la cavitación espontánea por fuerza bruta, no haciendo necesario el uso de teoría alguna (como la CNT). Pero para tratar un régimen de sobreestiramiento inferior (a presiones mayores), recurrimos como ya

hemos mencionado a la técnica de *Seeding*, que parte de un sistema de líquido con una burbuja ya presente. Las simulaciones espontáneas no permiten llegar al régimen donde se hacen los experimentos, pero nos permiten validar nuestras simulaciones de *Seeding*, que sí se superponen con las condiciones relevantes para los experimentos.

En las simulaciones de *Seeding* se calculó la presión promedio del líquido circundante con la expresión virial y el radio de la burbuja mediante perfiles de densidad radial. Alternativamente, se estimó el radio utilizando la definición de la superficie de división equimolar de Gibbs. Gibbs supone dos fases homogéneas separadas por una interfaz infinitesimalmente pequeña (plana), es decir las partículas pertenecen a una de las dos fases en coexistencia porque ninguna pertenece a la interfaz. Por ello con esta última definición, para determinar el radio de la burbuja, solo se requiere conocer el volumen de la caja de simulación, el número total de moléculas, la densidad del líquido y la densidad del vapor. Así pues con la presión de ambas fases *bulk* y el radio de la burbuja se aplicó la CNT para obtener estimaciones de la tasa de nucleación y de la energía libre interfacial. Se obtuvo una enorme variación en la tasa de nucleación (de 10^{-300} a $10^{10} \text{ m}^{-3} \text{ s}^{-1}$) en el intervalo de presión que va de -130 a -430 bar. La energía libre interfacial disminuye a medida que disminuye la presión. La definición de radio de Gibbs predice una disminución de la energía libre interfacial de alrededor de $0,5 \text{ mJ m}^{-2}$ por cada reducción de 100 bar en la presión, mientras que la definición de equidensidad predice aproximadamente el doble de eso. Ambos criterios para identificar el radio de la burbuja dan una tendencia similar en la tasa, aunque el criterio de Gibbs da valores más bajos porque predice energías libres interfaciales más altas.

Al comparar con los resultados de cavitación espontánea se encontró que el ajuste de los datos de *Seeding* obtenidos con el radio de equidensidad extrapolan mejor al régimen de cavitación espontánea. Por lo tanto, el radio de equidensidad parece ser más apropiado para describir la cavitación del agua.

Finalmente, se observa que nuestros datos comparan bien con las predicciones teóricas [111, 112] y con los experimentos de calentamiento isobárico [113] y enfriamiento isocórico en inclusiones de cuarzo [114, 115]. Sin embargo, encontramos discrepancias irreconciliables con otras técnicas experimentales como el enfriamiento isocórico tipo Berthelot o cavitación acústica [116, 117, 118, 119, 120, 121, 122]. Postulamos que podría haber nucleación heterogénea de burbujas en tales experimentos, dado que la cavitación ocurre a presiones mucho más altas que las predichas por nuestras simulaciones y las de la Ref. [106], realizadas a 296,4 K. En general, nuestro trabajo muestra una manera eficiente de investigar y comprender los factores que controlan y afectan a la cavitación de agua, a la vez que se obtiene información experimentalmente relevante, mediante simulaciones.

Como acabamos de ver, el *Seeding* puede proporcionar tasas de cavitación consistentes con las obtenidas por métodos independientes de la CNT. La aplicabilidad del *Seeding NVT* ya ha sido demostrada para otras transiciones además de la cavitación que acabamos de ver, en particular para la nucleación de cristales,

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pero siempre para sistemas de un solo componente [97]. Tampoco el *Seeding NpT* se ha utilizado para estudiar la cavitación en sistemas multicomponentes, aunque si se ha usado para estudiar la nucleación de cristales en varios sistemas multicomponentes, tales como la cristalización de hielo y NaCl a partir de disoluciones acuosas que ya hemos visto [77, 103, 39]. Hablando en términos generales, los estudios de simulación de cavitación de burbujas a partir de mezclas binarias son bastante escasos y a menudo este fenómeno se ha estudiado teóricamente, por ejemplo, en el marco de la teoría del funcional de la densidad o en el marco de la CNT [123, 124, 125, 126]. Sin embargo, la extensión de la CNT a sistemas multicomponentes no ha sido sencilla [127, 128, 129]. Varias de las formulaciones propuestas conducen a resultados no físicos, especialmente para mezclas no ideales, lo que se ha atribuido al hecho de que el efecto de la curvatura en la energía libre interfacial no se puede ignorar [129].

Por ello el siguiente paso, tras haber aplicado el *Seeding NVT* por primera vez a un sistema complejo, fue aplicarlo a un sistema binario sencillo. Para ello elegimos como sistema una mezcla simétrica parcialmente miscible de Lennard-Jones truncado y desplazado (TSF-LJ), a una temperatura en la que el líquido es miscible y para la cual existen datos disponibles previos para el modelo puro de TSF-LJ [36, 37]. En estas condiciones, esperamos que el comportamiento de cavitación siga un mecanismo similar al del sistema puro. Esta es una de las mezclas más simples que se pueden imaginar, y esto la convierte en un sistema modelo ideal en el que investigar la aplicabilidad del método antes de abordar la nucleación en sistemas binarios más complejos. Sintetizando, el objetivo principal que se persigue en el trabajo que compone el capítulo 9 es ilustrar la aplicabilidad de *NVT Seeding* para el estudio de la transición líquido-vapor en mezclas.

Un aspecto que requiere especial cuidado al implementar *Seeding* es la elección de un criterio apropiado para determinar el tamaño de la burbuja. Aquí, al igual que en el capítulo 8, utilizamos tanto el radio de equidensidad como el radio de equimolaridad (o superficie de división de Gibbs). Consistentemente con trabajos previos [35, 36, 37, 40], los radios de equidensidad obtenidos son sistemáticamente más pequeños que los radios de Gibbs, lo que conduce a una barrera de energía libre inferior y una tasa de cavitación mayor. Al comparar las tasas de nucleación derivadas de ambos radios con las obtenidas de simulaciones de cavitación espontánea, el radio de Gibbs proporciona tasas más congruentes. La misma tendencia se observó en el modelo puro de TSF-LJ [35, 36, 37], pero a metastabilidades más bajas, las tasas calculadas con los radios de equidensidad están más cercanas a las obtenidas por *Forward-Flux Sampling* y *Umbrella Sampling* [35]. Para la nucleación de gotas en el mismo sistema, las tasas de nucleación de equidensidad también están más en acuerdo con los resultados de simulaciones de *Umbrella Sampling* [37]. Sin embargo, un estudio reciente que utiliza métodos de muestreo mejorados y la Teoría del Estado de Transición encontró resultados que están de acuerdo con los resultados obtenidos a partir de radios de Gibbs, y concluyen que el FFS da tasas sistemáticamente más altas [130, 18, 16]. Por lo tanto, concluimos que, para el modelo TSF-LJ a altas metastabilidades, cerca de

la región donde las simulaciones de fuerza bruta son factibles, los radios de superficie de división de Gibbs dan las tasas de nucleación correctas. Pero a bajas metastabilidades, donde se necesitan técnicas de simulación para eventos raros, la situación no está aún clara, ya que existen resultados contradictorios utilizando técnicas rigurosas [130].

En cualquier caso, las diferencias en las tasas de cavitación entre la mezcla simétrica y el sistema puro son mayores que las diferencias entre las tasas de *Seeding* utilizando diferentes criterios para determinar el tamaño de la burbuja. Por lo tanto, se pueden sacar conclusiones sobre la diferencia en el comportamiento de cavitación en los dos sistemas. A la misma diferencia de presión frente a la coexistencia, la burbuja crítica es más pequeña en la mezcla binaria que en el sistema puro. La razón es que la energía libre interfacial es aproximadamente un 25 % menor en la mezcla, es decir, el costo de energía libre de crear una burbuja es menor en la mezcla. Esto se relaciona con el hecho de que la temperatura crítica es menor en la mezcla que en el sistema puro [131, 132]. En las referencias [133, 37] se encontró que las barreras de energía libre a diferentes temperaturas para la nucleación de burbujas y gotas colapsan en una sola curva cuando se representan como una función de la metaestabilidad escalada, $\Delta\mu/\Delta\mu_{spin}$, donde $\Delta\mu$ es la diferencia de potencial químico entre el líquido metaestable y la coexistencia, y $\Delta\mu_{spin}$ es la diferencia de potencial químico entre el espinodal y la coexistencia. Los hallazgos de este trabajo sugieren que esta conclusión también se puede extender a las mezclas, al menos para pequeñas desviaciones de las interacciones cruzadas de las interacciones entre los mismos componentes, como las consideradas aquí. Se muestra que al comparar el sistema puro con el binario al mismo grado de metaestabilidad escalada, la barrera de energía libre es similar en ambos sistemas, es decir que el costo de crear una burbuja es similar en los líquidos puro y binario de LJ a la misma metaestabilidad.

Al finalizar la lectura de estos capítulos, se llegará al capítulo 10, el cual ofrece una mirada retrospectiva y una lista de los logros más significativos de la tesis.

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Capítulo 4

Fundamento teórico

En este capítulo daremos una introducción para presentar las principales herramientas teóricas utilizadas en esta tesis. Por orden: en la sección 4.1 se discuten los términos de estabilidad, metaestabilidad y equilibrio termodinámico; en la sección 4.2 se introduce y detalla el fenómeno físico de la nucleación, el eje central de esta tesis doctoral; en la sección 4.2.1 se explica la Teoría Clásica de Nucleación (CNT), la teoría más extendida para explicar dicho fenómeno; en la sección 4.2.2 se desarrolla matemáticamente cómo obtener la barrera de energía libre de nucleación (ΔG) a través de la termodinámica de interfases curvas y su relación con la CNT; en la sección 4.2.3 se desarrolla matemáticamente como obtener la tasa de nucleación (J) a través de la CNT, uno de los parámetros más importantes a la hora de describir la nucleación, ya que es el número de núcleos críticos que se forman por unidad de volumen y de tiempo; en la sección 4.2.4 se describe como calcular la tasa de nucleación a partir del tiempo promedio de nucleación aplicando la distribución de Poisson para eventos raros y, por último, en la 4.3 se describen los diferentes modelos de potencial que se utilizan en esta tesis doctoral.

4.1 Estabilidad, metaestabilidad y equilibrio termodinámico

Un diagrama de fases nos muestra gráficamente cuál es la fase estable (aquella con menor potencial químico) para unas determinadas condiciones termodinámicas (dadas por variables intensivas), por ejemplo para cada valor de concentración, temperatura y/o presión.

Una fase es metaestable cuando se encuentra en condiciones termodinámicas donde otra fase es más estable que esta. Un ejemplo es el agua subenfriada donde encontramos el líquido a temperaturas por debajo de la temperatura de fusión del hielo a la presión considerada. Otro ejemplo sería el agua sobrecalentada, donde encontramos la fase líquida a temperaturas por encima de la temperatura de ebullición a una determinada presión.

En un estado termodinámico dado, dos (o más) fases (*I*, *II*) están en equilibrio cuando el potencial químico de todos los componentes del sistema (dos en

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los casos que vamos a estudiar) son iguales en las fases que coexisten:

$$\begin{aligned}\mu_1^I(p, T, x_1^I) &= \mu_1^{II}(p, T, x_1^{II}) \\ \mu_2^I(p, T, x_2^I) &= \mu_2^{II}(p, T, x_2^{II})\end{aligned}\tag{4.1}$$

donde μ_i^α y x_i^α son, respectivamente, el potencial químico y la fracción molar del componente i en la fase α .

La regla de fase de Gibbs impone restricciones en el número de fases que pueden coexistir y se aplica tanto a sistemas de un solo componente como a múltiples componentes. Afirma que para un sistema con C componentes y P fases, el número de variables independientes o grados de libertad F viene dado por:

$$F + P = C + 2.\tag{4.2}$$

Como resultado, en sistemas de un solo componente ($C = 1$), y una sola fase ($P = 1$), el número de grados de libertad F es 2, lo cual quiere decir que uno puede modificar libremente p y T y seguir teniendo únicamente una sola fase. Por otro lado si en un sistema de 1 componente ($C = 1$), tenemos dos fases $P = 2$, entonces F es 1. Podemos elegir la T (y el sistema determinará el valor de p para alcanzar el equilibrio), o podemos elegir p (y el sistema determinará el valor de T de equilibrio), puesto que solo tenemos un grado de libertad. No es posible fijar p y T pretendiendo que el sistema siga teniendo dos fases, ya que este evolucionará hacia una única fase. Esto explica por qué en un sistema de un solo componente, como el del capítulo 8, no se puede estabilizar una interfaz en un sistema puro en simulaciones NpT . Pero en el colectivo NVT , solo la temperatura está fija ($F = 1$), de modo que en estas condiciones pueden coexistir dos fases de un sistema de un solo componente [1].

Por el contrario, en un sistema de dos componentes ($C = 2$), como los que encontramos en los capítulos 5, 6, 7 y 9, podemos tener dos fases en equilibrio y modificar p y T de forma independiente, puesto que tenemos ahora dos grados de libertad ($F = 2$). En este caso, las composiciones de las dos fases en coexistencia evolucionan hasta que los potenciales químicos de cada componente son iguales en las dos fases (ecuación 4.1). Aunque hemos escrito la condición de igual potencial químico del componente 2 en términos de su fracción molar (x_2^I y x_2^{II}), también podría haber sido escrita en términos de las fracciones molares de componente 1 (x_1^I y x_1^{II}) porque las fracciones molares suman uno en cada fase ($x_1^I + x_2^I = 1$ y $x_1^{II} + x_2^{II} = 1$). Por lo tanto, en sistemas de dos componentes, solo hay una variable independiente que ajusta las composiciones de las dos fases de coexistencia.

4.2 El proceso de nucleación

El proceso de nucleación es el primer paso de una transición de fase de primer orden, que implica la formación de un embrión de fase estable en una fase termodinámicamente metaestable [2]. Cuando hablamos de embrión nos referimos

a un agregado o clúster de partículas de la fase nueva/estable, también se conoce como núcleo. Cuando este agregado es lo suficientemente grande, es decir cuando supera un tamaño crítico se produce un crecimiento irreversible de la fase estable completando el cambio de fase del sistema. Al clúster que tiene dicho tamaño se le conoce como núcleo crítico.

Este proceso es activado, es decir se requiere superar una energía para que tenga lugar. La altura de la barrera de energía libre necesaria para este proceso depende de qué tan lejos se encuentren las condiciones de la fase metaestable de la línea de coexistencia. Cerca de la línea de coexistencia, la barrera de energía libre es alta (se puede considerar infinita en las condiciones de coexistencia) y el tamaño del clúster crítico es grande. Sin embargo, a medida que nos alejamos de esta línea, la fuerza motriz para que se produzca la nucleación aumenta, lo que provoca una disminución drástica en la altura de la barrera y el tamaño de los embriones necesarios para la transformación de fase.

Existen dos tipos de nucleación. Por un lado, la nucleación homogénea en la que un clúster de la fase estable suficientemente grande para crecer se forma a partir de fluctuaciones espontáneas en la fase metaestable (que en algún momento son suficientemente grandes para superar la barrera energética). Y por otro la nucleación heterogénea, la cual se facilita por la presencia de impurezas, superficies sólidas o de la fase estable que disminuyen la barrera de energía libre, ya que las partículas se agregan sobre ellas. La superficie proporciona un lugar de anclaje para las partículas individuales, lo que facilita la formación de un núcleo. Como veremos en detalle en la sección 4.2.2, la razón de esto es que la creación de una interfaz entre la fase metaestable y la nueva fase estable requiere de un aporte energético y en el caso de la nucleación heterogénea la interfase a crear es menor.

Esta tesis se centra en procesos de nucleación homogénea. A priori puede parecer que en la naturaleza los procesos de nucleación son de tipo heterogéneo, pero hay ejemplos muy importantes de nucleación homogénea como es la congelación de microgotas en las nubes. Por tanto, entender la nucleación homogénea ayudaría a entender mejor las características de las nubes y su formación, como influyen en el albedo (reflejo del sol) y por tanto en la temperatura de la Tierra, lo que es relevante cuando hablamos de un tema tan candente en la actualidad como es el cambio climático [3]. Además para entender el proceso de nucleación heterogénea hay que entender primero muy bien la nucleación homogénea, y este proceso aún presenta muchas incógnitas.

En particular esta tesis trata los casos de la formación de burbujas o cristales a partir de un líquido.

Para convencer al lector de la importancia de estos procesos a continuación se profundiza en su relevancia. Empezamos por el proceso de formación de cristales en una disolución supersaturada (es decir, un sistema en el que la cantidad del soluto disuelta es mayor que la cantidad que puede disolverse espontáneamente en las condiciones a las que se estudia). En este caso, la nucleación se refiere al momento en que a partir de un líquido metaestable los iones, átomos o moléculas individuales comienzan a formar grupos estables y ordenados, formando los pri-

meros núcleos de cristales. El conocimiento de este mecanismo es importante en medicina porque la agregación de proteínas se relaciona con enfermedades como el Alzheimer; la cristalización desde disolución se usa con gran frecuencia en procesos industriales como la separación o purificación de sustancias; la nucleación de cristales moleculares también tiene enorme importancia para las farmacéuticas, ya que afecta al diseño y producción de medicamentos debido a la necesidad de controlar el polimorfo cristalino que se obtiene (porque de esto depende la eficacia y disminución de efectos secundarios del medicamento) [4]; a su vez es interesante para la industria, ya que debe controlarse la formación de depósitos en cañerías conductoras de líquidos, como el agua, disoluciones acuosas o el petróleo. Por otro lado la formación de burbujas (gas) en líquidos metaestables (en este caso sobrecalentado o hipopresurizado), es también importante, por ejemplo en el diseño de hélices o procesos de destilación para evitar daño en los componentes, pérdida del rendimiento o ruido [5, 6, 7] y también en geología debido al vulcanismo [8], la erosión, la cavitación acústica [7] o la ebullición explosiva [5].

El mecanismo de nucleación determina la velocidad y el producto de la transición de fase. Por ello, para predecir y controlar estos procesos, se necesita un gran entendimiento y conocimiento sobre la nucleación. Este fenómeno presenta dificultades para ser estudiado experimentalmente pues es un evento estocástico, es decir se desconoce de antemano cuando o donde va a suceder, a su vez es un evento perteneciente a la nanoescala temporal y física y a veces en condiciones difíciles de alcanzar. Las simulaciones por ordenador se han venido usando en las últimas tres décadas para estudiar la nucleación, por tener acceso a la nanoescala [4, 9, 10, 11].

Para simplificar el texto hasta ahora y en algunas de las próximas secciones, nos hemos referido a la nucleación de forma general para englobar todos los cambios de fase. Cuando hablamos de cavitación tratamos la formación de burbujas en un líquido. A su vez en el caso de que el embrión de la fase estable sea un gas no se suele llamar núcleo sino burbuja. Tras haber definido la nucleación y haber matizado su importancia, se va a tratar su descripción desde un punto de vista teórico. Empezaremos describiendo cualitativamente la Teoría Clásica de Nucleación que es la más extendida para explicar el fenómeno de la nucleación (sección 4.2.1), luego desarrollaremos matemáticamente como obtener la barrera de energía libre de nucleación (sección 4.2.2), a continuación entraremos en cómo se define la tasa de nucleación descrita por la CNT, tratando la cinética de nucleación (sección 4.2.3), y por último explicaremos la forma más sencilla e intuitiva de obtener la tasa de nucleación que es por tratamiento estadístico a partir del tiempo promedio que tarda un sistema en nuclear (sección 4.2.4).

4.2.1 Teoría Clásica de Nucleación

La Teoría Clásica de Nucleación, con siglas CNT provenientes de inglés *Classical Nucleation Theory*, es el modelo teórico comúnmente utilizado para entender la nucleación homogénea de una nueva fase termodinámica estable en el seno de

una fase metaestable. Sus inicios datan de 1926 de la mano de Volmer y Weber [12], está basada en las ecuaciones de Gibbs [13, 14], que calculaban el trabajo reversible para formar un núcleo. La teoría se fue completando con el trabajo de varios científicos como Becker y Döring que en 1935 aplicaron conceptos de la teoría del estado estacionario al problema de la nucleación para proponer una expresión teórica para la tasa de nucleación [15], como veremos en la sección 4.2.3. Inicialmente la CNT se formuló para tratar la condensación de vapor para formar un líquido, pero en el año 1949, Turnbull y Fisher aplicaron la teoría a transiciones líquido-sólido también [16].

La CNT considera tres parámetros fundamentales en la investigación de la nucleación: la energía libre de formación del clúster, su tamaño y la tasa de nucleación. Varios autores han aproximado el tamaño del núcleo crítico usando experimentos y simulaciones. Sin embargo, las simplificaciones de la CNT, pueden llevar a errores en la descripción de la nucleación en sistemas más complejos. Estas suposiciones son:

1. El núcleo se describe con las propiedades macroscópicas de la fase estable (densidad, estructura, composición).
2. El núcleo es esférico.
3. La interfaz es abrupta.
4. Aproximación capilar. Se supone que el valor de la energía interfacial no varía con el radio de curvatura del clúster, ni su tamaño y puede tomarse del valor de la interfase plana. Esta aproximación tiene sentido para núcleos grandes, pero no para los pequeños, donde la interfaz se presenta muy curvada. Realmente esta suposición puede omitirse en formulaciones avanzadas de CNT y no es estrictamente necesaria.

Sin embargo, estos supuestos pueden no ser válidos en ciertos casos, por lo que la teoría clásica de nucleación puede no ser aplicable en todos los escenarios. Por ello, aun cuando la CNT proporciona una interpretación cualitativa razonable de la nucleación, su fracaso para predecir adecuadamente los resultados experimentales en varios sistemas ha llevado a la necesidad de desarrollar teorías más complejas. Aún así la CNT todavía se utiliza como base para describir la nucleación, ya que se basa en información experimentalmente accesible y puede proporcionar estimaciones razonables. Nótese que es la aproximación 4 la que en muchos casos conduce a resultados erróneos de CNT. Cuando se permite que el valor de la energía interfacial varíe con el radio de curvatura del clúster los resultados mejoran ostensiblemente. Además, sin aumentar la complejidad de las expresiones teóricas, se puede extender la CNT obteniendo sus parámetros con simulación, lo que da origen al *Seeding*, técnica que se ha usado en esta tesis para estudiar la nucleación (capítulos 7, 8 y 9).

En resumen, esta teoría busca explicar cómo se forman nuevas fases en la materia y puede ser utilizada para estudios tanto teóricos como experimentales. En

las siguientes secciones detallaremos las diferentes deducciones que llevan a las ecuaciones de esta teoría, empezaremos deduciendo la barrera de energía libre de nucleación partiendo del formalismo termodinámico para interfases curvas que se relacionará al final con la CNT (sección 4.2.2), y luego se explicará como obtener la tasa de nucleación con la barrera de energía (sección 4.2.3).

4.2.2 Barrera de energía libre de nucleación

Hemos hablado de que la nucleación es un proceso activado, y que se necesita superar la barrera de energía libre de nucleación. En este apartado se va a definir esta energía y su desarrollo matemático. En el proceso de nucleación, una fluctuación espontánea del sistema adopta la energía libre necesaria para superar la barrera de energía libre de nucleación y formar la nueva fase.

En la nucleación partimos de un sistema homogéneo (*S.H.*) formado por líquido metaestable y en el momento en el que empieza a formarse un embrión de la fase estable tenemos un sistema inhomogéneo (*S.In.*), con un núcleo en el líquido. Queremos conocer la diferencia de energía libre de Gibbs (ΔG , barrera de energía libre) de estos sistemas, para ello primero vamos a ver cuál es la G de cada uno.

La ecuación fundamental de la termodinámica que describe la energía de Gibbs nos dice que:

$$dG = -SdT + Vdp + \sum_i \mu_i dN_i \quad (4.3)$$

donde S es la entropía, p es la presión, V es el volumen del sistema y μ_i es el potencial químico de la especie i con N_i número de partículas.

En un líquido homogéneo en equilibrio, podemos suponer que la presión y la temperatura son constantes, $dp = dT = 0$. Por lo tanto, podemos simplificar la ecuación 4.3 a:

$$dG_H = \sum_i \mu_i dN_i. \quad (4.4)$$

Integrando la ecuación 4.4 con respecto al número de partículas a lo largo de un proceso reversible y teniendo en cuenta que en un líquido homogéneo mono-componente en equilibrio todas las moléculas son idénticas, obtenemos la energía libre de *S.H.*:

$$G_H = \mu N. \quad (4.5)$$

Por otro lado para el *S.In.* usaremos la ecuación integrada 4.6 que relaciona la energía libre de Gibbs con la de Helmholtz (F).

$$G_{In} = F_{In} + pV \quad (4.6)$$

donde el volumen total del sistema viene dado por el volumen de la fase madre, la fase externa, que en este desarrollo se corresponde con el del líquido porque

en esta tesis siempre se trabaja con un líquido como fase externa y el de la nueva fase que puede ser un gas o un sólido, $V = V_l + V_n$. En condiciones de equilibrio, la presión del *S.In.* es igual a la del líquido homogéneo a igual potencial químico que el *S.In.*, $p = p_l$. Conocer la relación entre G y F es conveniente porque el núcleo estable en el colectivo canónico (NVT , número de partículas, volumen y temperatura constantes) (corresponde con el mínimo de energía de Helmholtz) es crítico (equilibrio inestable) en el isotérmico-isobárico (NpT , número de partículas, presión y temperatura constantes) (corresponde al máximo en la energía de Gibbs) como se demuestra en las referencias [17, 18, 19, 20] y en el capítulo 9. Es más sencillo evaluar la expresión para F al describir un equilibrio estable y luego relacionarla con G .

Desarrollando el término F_{In} para el equilibrio interfases curvas obtenemos [21]:

$$F_{In} = \mu_n N_n - p_n V_n + \mu_l N_l - p_l V_l + \mu_{exc} N_{exc} + \gamma A \quad (4.7)$$

donde γ es la energía libre interfacial, A es el área de la interfase, el subíndice n se refiere a la nueva fase, es decir al núcleo o embrión, l al líquido y exc a las partículas de exceso que son las que pertenecen a la interfase. La razón por la que $p_n \neq p_l$ es porque las separa una interfase curva. Aclarar que según el formalismo de Gibbs la interfase contribuye termodinámicamente, pero no tiene volumen. Como el sistema se encuentra en equilibrio termodinámico μ es homogéneo y por tanto $\mu_n = \mu_l = \mu_{exc}$, así pues podemos simplificar la ecuación 4.7 teniendo en cuenta que el número de partículas total en el sistema es $N_T = N_l + N_n + N_{exc}$:

$$F_{In} = N_T \mu - p_n V_n - p_l V_l + \gamma A. \quad (4.8)$$

Sustituyendo la ecuación 4.8 en la expresión 4.6 obtenemos la energía de Gibbs del *S.In.*:

$$G_{In} = N_T \mu - p_n V_n - p_l V_l + \gamma A + pV. \quad (4.9)$$

Finalmente podemos calcular la barrera de la energía libre de Gibbs para la nucleación como $\Delta G = G_{In} - G_H$ con las ecuaciones 4.9 y 4.5:

$$\Delta G = -p_n V_n - p_l V_l + \gamma A + p_l V = \gamma A - V_n \Delta p \quad (4.10)$$

donde $\Delta p = p_n - p_l$. Esta ecuación no tiene ninguna aproximación, para poder aplicarla lo único necesario es que el núcleo a tratar es que el sistema esté en equilibrio (estable o inestable) de modo que μ sea homogéneo. Podemos aplicar la ecuación 4.10 tanto en el colectivo NVT porque el sistema está en equilibrio estable, como en el NpT que cumple la mencionada condición también porque el núcleo está en equilibrio inestable (tiene un 50 % de probabilidades de fundir o crecer). Además esta ecuación no depende del criterio elegido para determinar la superficie divisoria (interfase) mientras haya congruencia entre los términos utilizados que sí dependen del criterio, que son A , V_n y γ . En el próximo apartado se tratarán las formas más extendidas de determinar la superficie divisoria.

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Cuando dentro de un fluido tenemos una burbuja de gas o una gota de fluido inmiscible esta adopta una forma esférica, minimizando la superficie de contacto entre fases. El lector puede recordar una situación en la que observó una gota de aceite en el seno de un vaso de agua o la liberación de burbujas de aire en un acuario para corroborar que efectivamente la gota o burbujas eran esféricas. Aún en el caso de ser un sólido el que se forma en la disolución se ha visto que normalmente cuando el clúster tiene un tamaño menor o en torno al del núcleo crítico se mantiene una forma esférica [22, 23]. Entonces, tomando el clúster crítico como esférico, la superficie o área de la interfase viene dada por la expresión matemática:

$$A = 4\pi R^2 \quad (4.11)$$

donde R es el radio del clúster de la fase estable y su volumen viene dado matemáticamente por:

$$V_n = \frac{4}{3}\pi R^3. \quad (4.12)$$

Sustituyendo las ecuaciones 4.11 y 4.12 en la ecuación 4.10, podemos expresar la barrera de energía libre de Gibbs como:

$$\Delta G = 4\pi R^2 \gamma - \frac{4}{3}\pi R^3 \Delta p. \quad (4.13)$$

Esta ecuación solamente es cierta y tiene sentido termodinámico cuando estamos en equilibrio, es decir cuando el radio del clúster es el del radio crítico. Como ya explicamos ΔG es invariante a cualquier elección arbitraria de la superficie divisoria. Es decir las magnitudes termodinámicas no dependen de una elección arbitraria de la superficie divisoria. Dado que Δp es un parámetro fijo, si ΔG debe permanecer fijo, entonces γ debe cambiar con la elección arbitraria de R . Por ello derivamos en R la ecuación 4.13 e igualamos a 0, $\left[\frac{d\Delta G}{dR}\right] = 0$ (los corchetes indican que es una derivada notacional, es decir un cambio en la elección arbitraria de la superficie divisoria sin que exista un cambio físico en el sistema):

$$\Delta p = \frac{2\gamma}{R} + \left[\frac{d\gamma}{dR}\right]. \quad (4.14)$$

La superficie divisoria, es decir dónde empieza y dónde acaba la interfase, que hace que se cumpla la ecuación de Young-Laplace es la de tensión. Esta toma R en el punto en el cual la γ es mínima, $\left[\frac{d\gamma}{dR}\right]_{R_s} = 0$, donde el subíndice s implica la superficie divisoria de tensión.

Como puede verse, cuando se elige como superficie divisoria la interfase de tensión R_s recuperamos la ecuación de Young-Laplace :

$$\Delta p = \frac{2\gamma_s}{R_s}. \quad (4.15)$$

Dado que tanto γ_s como R_s son positivos, Δp tiene que ser positivo también, lo que implica que la presión del núcleo es mayor que la presión de la fase que lo rodea.

Hemos explicado el desarrollo de estas ecuaciones partiendo desde un líquido metaestable para hacer más sencilla la explicación, aunque podría ser otro estado de la materia como por ejemplo un gas.

Barrera de energía libre de nucleación en la teoría clásica de nucleación

Las ecuaciones 4.10 y 4.13 son dos de las ecuaciones principales de la CNT, a pesar de que se han deducido a través del formalismo termodinámico para interfaces curvas sin entrar en postulados de la CNT. A pesar de que las ecuaciones 4.10 y 4.13 son estrictamente válidas cuando el núcleo es crítico, es decir cuando el sistema está en equilibrio, vamos a continuar la descripción suponiendo que se puede usar para cualquier tamaño de núcleo para poder describir el perfil de energía libre aproximado. Si hacemos ahora $\left(\frac{d\Delta G}{dR}\right)_{R^*} = 0$, donde el paréntesis implica un cambio físico en el tamaño del sistema y donde las variables Δp y γ se tratan como constantes que no dependen de R , obtenemos el máximo en el radio, que es el radio del clúster crítico R^* :

$$R^* = \frac{2\gamma}{\Delta p}. \quad (4.16)$$

Comparando las ecuaciones 4.15 y 4.16 concluimos que el valor de γ que hay que utilizar en CNT es γ_s , y el radio que hace máximo ΔG , es $R^* = R_s = R_s^*$. Lo cual implica que el máximo de la ecuación 4.13 como función de $R(R^*)$ ocurre precisamente en la superficie divisoria de tensión del clúster crítico. El valor de ΔG en dicho máximo es la barrera de energía libre de nucleación ΔG^* .

Sustituyendo la ecuación 4.16 en la ecuación 4.13 obtenemos la ecuación propuesta por Gibbs para describir la barrera de energía libre [25]:

$$\Delta G^* = \frac{16\pi\gamma_s^3}{3\Delta p^2}. \quad (4.17)$$

Si ahora queremos expresar ΔG^* en función de R en vez de γ_s , podemos usar la ecuación 4.16 (de Young-Laplace) para obtener la expresión:

$$\Delta G^* = \frac{2\pi\Delta p R_s^{*3}}{3}. \quad (4.18)$$

Las ecuaciones 4.10, 4.16, 4.17 y 4.18 son las que veremos en los capítulos 8 y 9 para la cavitación en la transición **líquido-vapor**. En este tipo de transición obtenemos R^* y Δp de nuestras simulaciones para obtener la barrera de energía libre de Gibbs. Para conocer el radio de la superficie divisoria de tensión debemos conocer ΔG , pero en los trabajos de esta tesis en los que empleamos la técnica de *Seeding* no conocemos ΔG , por ello usamos dos radios distintos que tratan de dar una aproximación razonable del radio crítico de la superficie de tensión R_s^* para obtener ΔG [24, 20]. Por un lado tenemos la superficie divisoria equimolar o de Gibbs, en este caso se considera que $N_{exc} = 0$ es decir no hay partículas que pertenezcan a la interfase, las partículas pertenecen a una fase u otra (se reparten

las partículas de la interfase a partes iguales entre fases). Por otro lado tenemos la superficie divisoria de equidensidad que se toma como el radio en el cual la densidad es un promedio de la de las dos fases que conforman el sistema. En cualquier caso, la superficie divisoria de la CNT es la de tensión y es en este caso cuando se cumple la ecuación de Young-Laplace 4.16. Por ello para estimar qué radio, de los propuestos para la técnica de *Seeding*, se acerca más al de tensión, se suelen comparar los resultados a los de otras técnicas.

Este formalismo se pensó inicialmente para explicar cómo una gota interactúa con el vapor. No obstante, también es aplicable a fases cristalinas, siempre que se tenga en cuenta que Δp representa el cambio en presión entre un sólido y un líquido *bulk* (es decir que se aplique la presión termodinámica y no la mecánica) cuando ambos tienen el mismo potencial químico [26].

En un fluido homogéneo, si conocemos su presión y temperatura, podemos determinar su densidad y potencial químico. En un sólido, conocer la presión y la temperatura no necesariamente implica conocer su potencial químico o densidad, ya que pueden presentar deformaciones elásticas en su estructura cristalina haciéndolo distinto del sólido macroscópico. Sin embargo, en el formalismo de Gibbs y en la ecuación de Young-Laplace la presencia de estrés en el sólido es irrelevante pues en el formalismo termodinámico lo que se considera como sólido de referencia es un sólido ideal bajo presión hidrostática y con el mismo potencial químico que el líquido que le rodea. Esta idea se propuso incluso en fases fluidas por Tolman, para aquellas gotas demasiado pequeñas donde la presión real del sistema podría diferir de la obtenida mediante el formalismo termodinámico [27] y ha sido extendida a sólidos en el trabajo de la Ref. [26].

ΔG^* para la transición líquido-sólido en la teoría clásica de nucleación

Ahora nos vamos a centrar en el estudio de un cambio de fase líquido-sólido, en este caso la expresión de ΔG^* que se suele usar es aproximada.

Mientras que las ecuaciones 4.17 y 4.18 son exactas y pueden utilizarse tanto para la cristalización como para la cavitación. Sin embargo, en el caso de la cristalización suele ser conveniente utilizar una forma aproximada que reemplaza Δp por $\Delta\mu$, la diferencia en potenciales químicos entre el *bulk* líquido y el *bulk* sólido cuando ambos están a la misma presión.

Para ello volvemos a la ecuación fundamental de la termodinámica 4.3 de donde obtenemos la relación entre Δp y $\Delta\mu$ a temperatura constante:

$$\left(\frac{\partial\mu}{\partial p}\right)_T = v_m \quad (4.19)$$

donde v_m representa el volumen por partícula. Para calcular la variación del potencial químico de una fase entre dos presiones, integramos esta expresión entre dichas presiones. Entonces para calcular la variación del potencial de la fase emergente, en este caso el sólido, entre la presión del líquido p_l (hemos visto que coincide con la del sistema global) y la del núcleo sólido p_n , usamos la siguiente expresión:

$$\Delta\mu_n = \int_{p_l}^{p_n} v_{m,n} dP. \quad (4.20)$$

Si suponemos que la densidad del sólido no cambia entre estas presiones, es decir que el sólido es incompresible, podemos expresar la diferencia de potencial químico como:

$$\Delta\mu_n = \mu_n(p_n) - \mu_n(p_l) = v_{m,n}(p_n - p_l). \quad (4.21)$$

Si ahora también suponemos que el núcleo es crítico, y que por tanto se cumple la igualdad de potenciales químicos entre las dos fases, $\mu_n(p_n) = \mu_l(p_l)$, a su correspondiente presión podemos reescribir la expresión:

$$\Delta\mu = \Delta\mu(p_l) = \mu_l(p_l) - \mu_n(p_l) = v_{m,n}\Delta p \quad (4.22)$$

donde hemos definido una nueva diferencia de potenciales químicos, $\Delta\mu$, que es la que se usa en la CNT y es la resta entre el potencial químico del líquido y del sólido ambos en su forma *bulk* a la presión del líquido (que como vimos en el anterior apartado coincide con la del sistema global). Además la $\Delta\mu$ debe ser positiva, porque la fase emergente, en este caso fase sólida es la fase termodinámicamente estable y tendrá un menor potencial químico que el líquido. Notar también que $(v_{m,n})^{-1} = \rho_n$ es decir la inversa del volumen por partícula o molécula coincide con la densidad (expresada como número de partículas o moléculas por unidad de volumen).

Despejando Δp en la ecuación 4.22 y sustituyendo en las ecuaciones para la barrera de la energía libre de Gibbs de nucleación 4.10 y 4.17 que ahora se presentarían con la forma:

$$\Delta G = \gamma_s A - V_n \rho_n \Delta\mu = \gamma_s A - N_n \Delta\mu \quad (4.23)$$

$$\Delta G^* = \frac{16\pi\gamma_s^3}{3(\rho_n \Delta\mu)^2}. \quad (4.24)$$

Las ecuaciones de la CNT se pueden dar en dos formalismos distintos, la ecuación 4.10 está expresada con uno que es el que está en función de V_n y Δp y la ecuación 4.23 está expresada con el otro que es el que está en función de N_n y $\Delta\mu$. Para cambiar una ecuación de un formalismo al otro únicamente tenemos que usar la ecuación 4.22 como acabamos de ver.

En esta tesis se tratará la nucleación de un sólido en disolución en el capítulo 7 y para monitorizar el tamaño del núcleo usaremos su número de partículas, N_n , por ello vamos a reescribir la ecuación 4.23 en función de este parámetro que de ahora en adelante para simplificar se denominará N . Para ello primero vamos a definir el volumen y el área del núcleo esférico en función de N :

$$V_n = \frac{N}{\rho_n} \quad (4.25)$$

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si ahora combinamos las ecuaciones 4.12 y 4.25 podemos despejar la equivalencia entre R y N :

$$R = \sqrt[3]{\frac{3N}{4\pi\rho_n}}. \quad (4.26)$$

A continuación sustituimos la ecuación 4.26 en la ecuación 4.11 para obtener el área A en función de N :

$$A = (36\pi)^{1/3} \left(\frac{N}{\rho_n}\right)^{2/3}. \quad (4.27)$$

Insertando la ecuación 4.27 en la ecuación 4.23 obtenemos la expresión para la barrera de energía libre en función de N :

$$\Delta G = \gamma_s (36\pi)^{1/3} \left(\frac{N}{\rho_n}\right)^{2/3} - N\Delta\mu. \quad (4.28)$$

Para eliminar la γ_s de la ecuación, podemos obtener el valor del tamaño del clúster crítico, N^* , de la anterior ecuación. El máximo de la curva de ΔG coincide con el tamaño del núcleo crítico, N^* , y matemáticamente se obtiene según $\frac{\partial \Delta G}{\partial N} = 0$. El clúster crítico es estable en el colectivo NVT (equilibrio estable) y tiene un 50% de probabilidades de fundir o crecer en el NpT (equilibrio inestable). Así presentamos la expresión del número de partículas que componen el clúster crítico:

$$N^* = \frac{32\pi\gamma_s^3}{3(\Delta\mu)^3\rho_n^2}. \quad (4.29)$$

Despejando γ_s^3 de la ecuación 4.29 e insertándolo en la ecuación 4.24 obtenemos la ecuación para la barrera de energía del clúster crítico que únicamente depende del tamaño del núcleo crítico y la diferencia de potenciales entre líquido y sólido. Esta expresión es la que usaremos en el capítulo 7:

$$\Delta G^* = \frac{N^*\Delta\mu}{2}. \quad (4.30)$$

Si nos fijamos en las ecuaciones 4.23, 4.24 y 4.28 observamos que en todos los casos hay dos términos y al aumentar el tamaño del núcleo de la nueva fase: uno disminuye el valor de ΔG , favoreciendo la nucleación (depende de $\Delta\mu$), y otro aumenta el valor de ΔG con el tamaño del clúster dificultando la nucleación (depende de γ). El término favorable es un término de *bulk* (pues los parámetros se sacan del *bulk* de la sustancia) y es la fuerza motriz de la nucleación, pues mide el grado de metaestabilidad del sistema con respecto a la fase termodinámicamente estable. Por tanto una mayor metaestabilidad favorece que se produzca la nucleación. El término desfavorable es un término de superficie, porque depende del área de la interfase y de la superficie divisoria de tensión. Por tanto nos indica el coste

energético de crear una interfase. En la figura 4.1 se representan los dos términos de la ecuación 4.13 y la ΔG resultante de ellos.

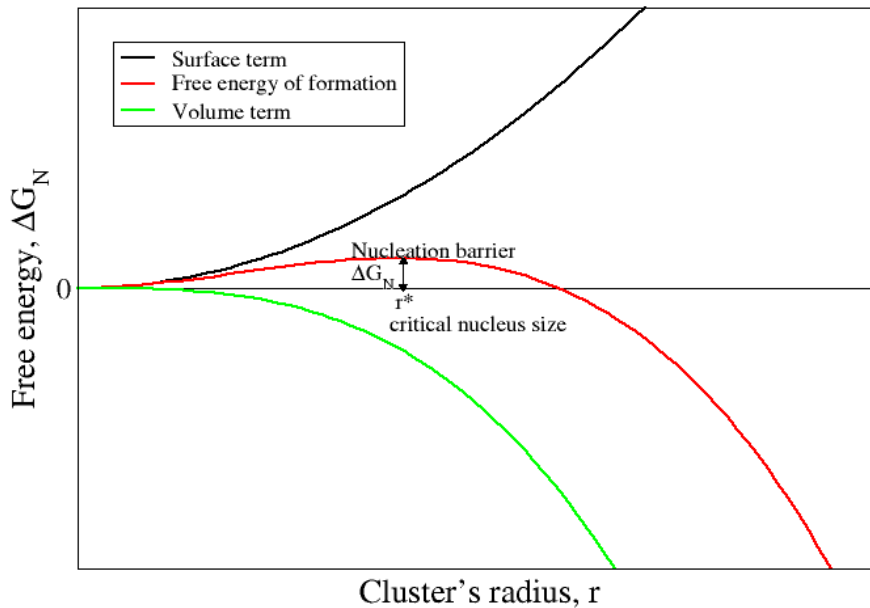


Figura 4.1. Esquema sobre la dependencia de la energía libre con el radio del núcleo en el marco de la CNT. Se puede observar la contribución de la energía interfacial o del término de superficie (desfavorable) en negro, y el término de *bulk* (favorable) en verde y el resultado de su suma, que es la energía libre de nucleación, en rojo.

4.2.3 Cinética de nucleación y tasa de nucleación a través de la CNT

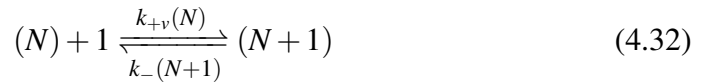
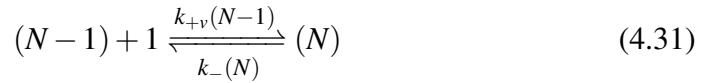
Vamos a describir la cinética de nucleación partiendo de que podemos identificar el número de partículas que componen los núcleos formados de fase estable en la fase metaestable, esto es necesario para poder describirla mediante ecuaciones cinéticas. Así pues exponemos la cinética de la reacción con ecuaciones que determinan cómo el núcleo gana o pierde partículas, tras hacer tres suposiciones [28]:

- No hay memoria, y por tanto no se tiene en cuenta la historia del clúster, es decir cómo y cuánto ha cambiado su tamaño. Así podemos decir que no hay correlación entre los eventos que modifican el tamaño del núcleo.

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- La temperatura es constante. Vamos a usar constantes cinéticas para caracterizar los eventos de adición o pérdida de partículas del clúster, esto implica implícitamente que la temperatura no puede cambiar durante la nucleación. Cuando el clúster cambia su tamaño produce o absorbe calor, vamos a suponer que la temperatura de este se equilibra entre colisiones (el calor difunde muy rápido). O dicho de otra manera el equilibrio termodinámico entre fases se alcanza de forma instantánea.
- El crecimiento o decrecimiento del clúster se produce a través de la adición o pérdida de monómeros. Esto implica que ignoramos las colisiones entre clusters. Esta aproximación será más razonable por ejemplo a bajas supersaturaciones o en el caso de la condensación a bajas temperaturas.

Teniendo en cuenta dichas aproximaciones podemos describir las reacciones cinéticas de crecimiento desde un tamaño del clúster $N - 1$ y N , en equilibrio con el correspondiente decrecimiento:



donde $k_{+v}(N)$ es la tasa a la cual un clúster de tamaño N gana una partícula (constante cinética de crecimiento) y $k_-(N)$ la tasa a la cual un clúster de tamaño N pierde una partícula (constante cinética de decrecimiento). Nótese que en las anteriores ecuaciones la cantidad de partículas que forman el clúster viene entre paréntesis. Vemos que la constante cinética de crecimiento depende de la concentración de monómeros en el entorno, en el caso más simple será proporcional a dicha concentración. Por ello, para que la constante cinética no dependa del tiempo la concentración de monómero debe permanecer constante a lo largo del crecimiento del núcleo, por ejemplo teniendo sistemas grandes en comparación al núcleo que se forma, esta sería la cuarta aproximación. Suponiendo que la concentración de monómeros es constante, podemos definir una constante cinética efectiva, $k_+(N) = k_{+v}(N)n(1)$, que va a ser la que usemos de ahora en adelante.

Ahora a través de estas ecuaciones cinéticas acopladas podemos describir el cambio de las densidades numéricas $n(N, t)$ para clusters de tamaño N a tiempo t según:

$$\frac{\partial n(N, t)}{\partial t} = k_+(N-1)n(N-1, t) - k_-(N)n(N, t) - k_+(N)n(N, t) + k_-(N+1)n(N+1, t). \quad (4.33)$$

Esta ecuación nos indica como evoluciona la distribución de tamaños de clúster con el tiempo. A continuación definimos la tasa neta dependiente del tiempo $J(N + \frac{1}{2}, t)$ como la frecuencia o el ritmo a la que clusters de tamaño N se convierten en clúster de tamaño $N + 1$:

$$J(N + \frac{1}{2}, t) = k_+(N)n(N, t) - k_-(N+1)n(N+1, t) \quad (4.34)$$

de manera que podemos escribir el cambio de las densidades numéricas con respecto al tiempo sustituyendo la ecuación 4.34 en la 4.33:

$$\frac{\partial n(N, t)}{\partial t} = J\left(N - \frac{1}{2}, t\right) - J\left(N + \frac{1}{2}, t\right). \quad (4.35)$$

Continuamos introduciendo una quinta aproximación, la del estado estacionario, de forma que la población del tamaño de los clusters no dependa del tiempo. Ahora la tasa neta de crecimiento de clusters J no depende del tamaño ni del tiempo, es decir que $J = J(N - \frac{1}{2}, t) = J(N + \frac{1}{2}, t)$. Es conveniente introducir una función f mediante una relación recursiva para que cada término venga definido como una función de los anteriores:

$$f(N+1) = \frac{k_+(N)f(N)}{k_-(N+1)} \quad (4.36)$$

definiendo $f(1) = 1$. Si analizamos la dependencia de $f(N)$ con N podemos reescribir la ecuación 4.36 con un productorio:

$$f(N) = \prod_{i=1}^{N-1} \frac{k_+(i)}{k_-(i+1)} \quad (4.37)$$

donde la relación $\frac{k_+(i)}{k_-(i+1)}$ es la tasa de crecimiento a la cual un clúster de N partículas gana una partícula dividido entre la tasa de decrecimiento a la cual un clúster de $N+1$ partículas pierde una. En condiciones de coexistencia si N es suficientemente grande se igualan ambas tasas y por tanto $f(N) = 1$. Pero para estudiar la nucleación se parte de condiciones de metaestabilidad, el sistema tiende a formar la fase termodinámicamente estable y por ello para N suficientemente grande $f(N) > 1$. Además para cada incremento en 1 de N , $f(N)$ tiene que crecer en más de 1, es decir $f(N)$ tiene un crecimiento exponencial con N .

Conociendo esta información, volvemos al parámetro que nos interesa. Reescribimos la tasa de nucleación dividiendo la ecuación 4.34 por $k_+(N)f(N)$ y usando la ecuación 4.36, obtenemos:

$$\frac{J}{k_+(N)f(N)} = \frac{n(N)}{f(N)} - \frac{n(N+1)}{f(N+1)}. \quad (4.38)$$

Ahora sumamos esta ecuación desde $N = 1$ hasta un valor superior $N \uparrow$ y como es una serie telescópica observamos que todos los términos menos el primero y el último se cancelan (recordemos también que $f(1) = 1$):

$$J \sum_{N=1}^{N \uparrow} \frac{1}{k_+(N)f(N)} = n(1) - \frac{n(N \uparrow)}{f(N \uparrow)}. \quad (4.39)$$

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Como hemos supuesto que la concentración de monómeros (densidad numérica de la fase metaestable) es constante y es muy superior a la de agregados de partículas, está claro que $n(1) \gg n(N \uparrow)$ y podemos despreciar el último término de la ecuación 4.39. Además como $f(N)$ tiene un crecimiento exponencial con N y $k_+(N)$ también es una función creciente, los sumandos decrecen exponencialmente con N . Realmente solo los primeros sumandos contribuyen y por ello cuando tenemos un valor de N lo suficientemente grande obtenemos el mismo valor que si hubiésemos supuesto $N \rightarrow \infty$, y podemos despejar la tasa de nucleación como:

$$J = \frac{n(1)}{\sum_{N=1}^{\infty} \frac{1}{k_+(N)f(N)}}. \quad (4.40)$$

La CNT se formuló inicialmente para condensación en gases diluidos o cristalización desde disoluciones diluidas, nos vamos a centrar en el primer caso aunque el segundo es análogo. En estos casos la constante de crecimiento del clúster k_+ depende como veremos del tamaño del clúster y de la densidad del gas y por tanto de su presión (tanto para condensación como para cavitación). Por otro lado la k_- es independiente de la presión del gas. Sabiendo esto podemos reescribir la ecuación 4.37:

$$f(N) = \prod_{i=1}^{N-1} \frac{k_+(i)}{k_-(i+1)} \quad (4.41)$$

el productorio de la ecuación se identifica como la constante de formación del clúster. El cociente de constantes cinéticas de una reacción reversible es la constante termodinámica $\exp\left(\frac{-\Delta G}{k_B T}\right)$, entonces la constante de equilibrio termodinámico de esta reacción reversible es:

$$f(N) = \exp\left(\frac{-\Delta G(N)}{k_B T}\right) \quad (4.42)$$

donde $\Delta G(N)$ es la energía libre de Gibbs de nucleación que ya hemos obtenido en la sección 4.2.2 para la reacción de N monómeros formando un clúster de tamaño N . Si ahora sustituimos la ecuación 4.42 en la ecuación 4.40 queda como:

$$J = \frac{n(1)}{\sum_{N=1}^{\infty} \frac{1}{k_+(N) \exp\left(\frac{-\Delta G(N)}{k_B T}\right)}}. \quad (4.43)$$

A continuación tomamos la función que hay dentro de la exponencial:

$$g(N) = \frac{\Delta G(N)}{k_B T} \quad (4.44)$$

y la aproximamos con una serie de Taylor con términos de hasta segundo orden (aproximación de Laplace), el desarrollo está tomado en torno al máximo, que es el clúster crítico:

$$g(N) \approx g(N^*) + 0 + \frac{g''(N^*)(N - N^*)^2}{2} \quad (4.45)$$

donde $g''(N^*)$ es la segunda derivada de la función evaluada en N^* , que como se refiere a un máximo tendrá valor negativo:

$$g''(N^*) = -|g''(N^*)| = -\frac{|\Delta G''^*|}{k_B T}. \quad (4.46)$$

Ahora para eliminar el sumatorio de la ecuación 4.43, vamos a llevar a cabo unas aproximaciones matemáticas. Los términos de la suma son más grandes cuando el denominador es mínimo, es decir cuando el tamaño del clúster se acerca al del núcleo crítico, N^* . Y cuando igualamos la derivada del denominador con respecto al tamaño del clúster (es decir el mínimo del denominador) a cero obtenemos el tamaño del núcleo crítico. Además la k_+ varía muy lento al alejarse de este tamaño y por tanto vamos a considerar la constante cinética del choque entre monómeros y el núcleo crítico, k_+^* . Tras esto podemos aproximar el sumatorio a una integral, es decir suponemos una variación continua del tamaño del núcleo. El sumatorio de la expresión 4.43 con los mencionados cambios quedaría con la forma:

$$\frac{1}{k_+^*} \int_{-\infty}^{\infty} \exp(g(N^*)) \exp\left(-\frac{|g''(N^*)|(N - N^*)^2}{2}\right) d(N - N^*). \quad (4.47)$$

Si N^* es lo suficientemente grande será una buena aproximación pues varios términos de N contribuyen al sumatorio. Una integral de Gauss, se resuelve según:

$$\int_{-\infty}^{\infty} \exp\left(-\frac{|g''(N^*)|(N - N^*)^2}{2}\right) d(N - N^*) = \sqrt{\frac{2\pi}{|g''(N^*)|}}. \quad (4.48)$$

Sustituyendo las ecuaciones 4.48, 4.44 y 4.46 en la expresión 4.47 y resolviendo la integral, obtenemos:

$$\frac{1}{k_+^*} \exp\left(\frac{\Delta G^*}{k_B T}\right) \sqrt{\frac{2\pi k_B T}{|\Delta G''^*|}}. \quad (4.49)$$

Teniendo en cuenta las mencionadas aproximaciones podemos reescribir la ecuación 4.43 sustituyendo el sumatorio por la expresión 4.49:

$$J = n(1)k_+^* \sqrt{\frac{|\Delta G''^*|}{2\pi k_B T}} \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (4.50)$$

tener en cuenta que evaluamos ΔG^* en su máximo, es decir en la energía correspondiente al núcleo crítico con tamaño N^* , también k_+^* es para el núcleo

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crítico. El término de la raíz se conoce como factor de Zeldovich, Z [29]:

$$Z = \sqrt{\frac{|\Delta G''|^*}{2\pi k_B T}} \quad (4.51)$$

es la inversa del ancho de la barrera de energía libre de Gibbs a aproximadamente un $k_B T$ del máximo en altura. Nos da la probabilidad de que un clúster al atravesar el máximo de la barrera crezca sin atravesar de nuevo el máximo de la barrera (decreciendo), toma por tanto valores entre 0 y 1. No debemos confundir esta probabilidad con la probabilidad a tiempos infinitos de que un clúster en el NpT crezca una vez alcanzado el máximo de la barrera, que es 0.5. Ya que a tiempos cortos nos encontraremos que el núcleo oscila en el máximo de un lado a otro. La tasa de nucleación viene dada entonces por la ecuación:

$$J = n(1)k_+^* Z \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.52)$$

Aunque normalmente se dice que el prefactor cinético viene dado por todo menos el término exponencial, la realidad es que estrictamente hablando el término cinético es $k_+^* Z$. Este término tiene unidades de frecuencia, porque Z es adimensional y k_+^* es una constante cinética de primer orden. $k_+^* Z$ nos da la inversa del tiempo que requiere un clúster para escapar del máximo de la barrera, si entendemos como máximo de la barrera la curva que engloba el máximo de ΔG^* y hasta un $k_B T$ por debajo aproximadamente. Siguiendo esta explicación, $n(1) \exp\left(\frac{-\Delta G^*}{k_B T}\right)$ es el término termodinámico y si nos fijamos bien nos damos cuenta de que es la concentración de clusters críticos en la disolución, y sus unidades son de la inversa del volumen. Así recuperamos correctamente las unidades de la tasa de nucleación, que son inversa de tiempo y volumen.

Partiendo de la ecuación 4.10 y sustituyendo las ecuaciones 4.27 y 4.25 podemos expresar la barrera de energía libre de Gibbs en función de N (sería una ecuación análoga a la ecuación 4.13 pero en función de N y no de R):

$$\Delta G = \gamma_s (36\pi)^{1/3} \left(\frac{N}{\rho_n}\right)^{2/3} - \frac{N}{\rho_n} \Delta p \quad (4.53)$$

en el caso de la condensación la nueva fase que se forma es líquido, por tanto ρ_n se refiere a la densidad del líquido ρ_l y N al número de partículas de líquido en la gota emergente.

La derivada segunda (con respecto al tamaño del clúster) de la barrera de energía se calcula a partir de la ecuación 4.53:

$$\Delta G'' = \frac{2\gamma_s}{9} \sqrt[3]{\frac{36\pi}{\rho_n^2 N^{*4}}}. \quad (4.54)$$

Sustituyendo γ_s con la ecuación 4.16 en la ecuación 4.54 e insertando esta en la ecuación eq.zeldo, el factor de Zeldovich quedaría como:

$$Z = \sqrt{\frac{\Delta p}{6\pi k_B T \rho_n N^*}}. \quad (4.55)$$

Sustituyendo ahora N^* con la ecuación 4.26 en la ecuación 4.55 reinterpretemos Z como:

$$Z = \sqrt{\frac{\Delta p}{8\pi^2 k_B T \rho_n^2 R_s^{*3}}} \quad (4.56)$$

y en el otro formalismo (usando la ecuación 4.22 sobre 4.55) como:

$$Z = \sqrt{\frac{\Delta \mu}{6\pi k_B T N^*}}. \quad (4.57)$$

Nos queda por ver cómo evaluar la constante cinética k_+^* que debe evaluarse cuando el núcleo es crítico. Vamos a suponer que las colisiones entre el núcleo esférico y los monómeros ocurren como en un gas ideal. En un gas ideal la frecuencia de colisiones de las partículas con una pared (es decir choques por unidad de tiempo y área) se expresa como:

$$C = \frac{\rho_g}{4} \langle v \rangle = \frac{\rho_g}{4} \sqrt{\frac{8k_B T}{\pi m}} = \rho_g \sqrt{\frac{k_B T}{2\pi m}} \quad (4.58)$$

donde ρ_g es la densidad del gas (número de partículas por unidad de volumen), $\langle v \rangle$ la velocidad promedio de las partículas y m es la masa de los monómeros. Si ahora queremos expresar los choques en función de la presión aplicamos que $p = \rho_g k_B T$:

$$C = \frac{p}{\sqrt{2\pi m k_B T}} \quad (4.59)$$

Así tomamos la constante cinética para gases ideales, que es simplemente la frecuencia de colisiones de la teoría cinética de los gases multiplicada por el área de superficie del clúster, A , (presentada en la ecuación 4.11):

$$k_+^* = CA = \rho_g \sqrt{\frac{k_B T}{2\pi m}} 4\pi R^{*2} \quad (4.60)$$

Esta demostración es para la condensación pero la ecuación 4.60 es igualmente válida para cavitación. En condensación vemos los choques del gas con la fase emergente, la gota líquida, y en cavitación del gas que forma la burbuja con la fase madre que lo rodea, el líquido.

A continuación obtenemos la expresión para calcular la tasa de nucleación en condensación, introduciendo las ecuaciones 4.56 y 4.60 en la ecuación 4.52:

$$J = \rho_g \sqrt{\frac{\Delta p}{8\pi^2 k_B T \rho_l^2 R_s^{*3}}} \rho_g \sqrt{\frac{k_B T}{2\pi m}} 4\pi R_s^{*2} \exp\left(\frac{-\Delta G^*}{k_B T}\right) = \rho_g \sqrt{\frac{\Delta p R_s^*}{\pi m} \frac{\rho_g}{\rho_l}} \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.61)$$

El paso que se hace en la última igualdad es agrupar los términos, y como resultado varios de ellos se cancelan. La expresión 4.61 también se puede dar en función de γ_s , sustituyendo Δp con la ecuación 4.16:

$$J = \rho_g \sqrt{\frac{2\gamma_s}{\pi m} \frac{\rho_g}{\rho_l}} \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.62)$$

A estas expresiones de la tasa de nucleación para condensación llegaron Blander y Katz [30].

A continuación vamos a ver cómo deberíamos expresar el prefactor cinético y la tasa de nucleación para las transiciones de fase que se estudian en esta tesis.

Prefactor cinético en cavitación

En la transición líquido-vapor usamos la expresión 4.60 para la constante cinética. Y las ecuaciones para el factor de Zeldovich 4.56. En este caso la nueva fase que se forma es vapor por tanto ρ_n se refiere a la densidad del gas ρ_g y N al número de partículas de vapor en la burbuja emergente.

$$J = \rho_l \sqrt{\frac{\Delta p}{8\pi^2 k_B T \rho_g^2 R_s^{*3}}} \rho_g \sqrt{\frac{k_B T}{2\pi m}} 4\pi R_s^{*2} \exp\left(\frac{-\Delta G^*}{k_B T}\right) = \rho_g \sqrt{\frac{\Delta p R_s^*}{\pi m}} \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.63)$$

El paso que se hace en la última igualdad es agrupar los términos, y como resultado varios de ellos se cancelan. La expresión 4.63 también se puede dar en función de γ_s , sustituyendo Δp con la ecuación 4.16:

$$J = \rho_l \sqrt{\frac{2\gamma_s}{\pi m}} \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.64)$$

En el capítulo 9 tratamos una mezcla en vez de un sistema puro, en él se tratarán los pormenores de cómo adaptar estas expresiones a mezclas. Aunque en el caso que tratamos usaremos las ecuaciones arriba propuestas pues tratamos con una mezcla en la que las diferentes partículas tienen la misma masa.

Si comparamos el prefactor cinético de cavitación y condensación, vemos que se diferencian en el valor de Z porque depende de la densidad de la fase emergente (se presenta dividiendo). Por otro lado comparando las tasas de nucleación y

teniendo en cuenta que la densidad del líquido es mayor que la del gas, deducimos que a igual ΔG^* la condensación es mucho más lenta que la cavitación.

Prefactor cinético para precipitación desde disolución

Este apartado lo vamos a adaptar al caso que se estudia en el capítulo 7, el de la precipitación de una sal desde su disolución iónica supersaturada. En este caso usamos la ecuación para el factor de Zeldovich 4.57. En este caso la nueva fase que se forma es sólida por tanto ρ_n se refiere a la densidad del sólido ρ_{ho_s} y N al número de partículas sólidas en el núcleo emergente.

En este caso k_+^* es la frecuencia de adhesión de los iones, que vamos a estimar de dos formas:

1. Se ha demostrado que k_+^* está limitada por la desolvatación y en este caso se puede expresar como [31, 32]:

$$k_+^* = D_{des} = 4\pi R^2 k_s \sigma_s \rho_{ions}, \quad (4.65)$$

donde k_s es una constante cinética de segundo orden de la adhesión de iones, σ_s es la concentración superficial de sitios de adhesión y ρ_{ions} es la concentración de iones en la disolución. El parámetro de adhesión, $k_s \sigma_s$ se puede calcular como la pendiente de la raíz cúbica del tamaño del núcleo frente al tiempo. Cabe remarcar que estas magnitudes apenas dependen del tamaño del clúster [32].

2. Auer y Frenkel proponen calcular la frecuencia de adhesión como:

$$k_+^* = D_{AF} = \frac{\langle (N_{ions}(t) - N_{ions}(0))^2 \rangle}{2t}, \quad (4.66)$$

donde $N_{ions}(t)$ es el número de iones del núcleo crítico en función del tiempo y $N_{ions}(0)$ es su valor inicial. Así pues, esta expresión requiere evaluar la pendiente del desplazamiento cuadrático medio del tamaño del núcleo. Además esta expresión se puede aplicar también a las transiciones líquido-gas.

D_{AF} se obtiene directamente de las simulaciones y D_{des} es una expresión más teórica, pero como veremos en el capítulo 7 son del mismo orden de magnitud. Teoría y simulación dan resultados similares. Al final la tasa de nucleación quedaría como:

$$J = \rho_{ions} k_+^* \sqrt{\frac{\Delta\mu}{6\pi k_B T N^*}} \exp\left(\frac{-\Delta G^*}{k_B T}\right). \quad (4.67)$$

4.2.4 Tasa de nucleación a través del tiempo promedio que tarda en nuclear el sistema

Normalmente la característica principal a estudiar en el principio de una transición de fase desde una fase metaestable es la tasa de nucleación, J [33]. Para ello se

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puede empezar por explicar la forma más sencilla y directa de estimar J , que es estudiando el tiempo que tarda en producirse el evento de la nucleación y aplicando el correspondiente tratamiento estadístico como vamos a explicar a continuación.

Hemos visto que para que se produzca la nucleación debemos sobrepasar una barrera de energía. Tras esto el núcleo crece rápidamente hasta que el sistema alcanza un estado estacionario (las características del sistema no varían con el tiempo). En este caso la formación de un núcleo de fase nueva en un sistema metaestable es un evento estocástico del cual no se conoce el momento o el lugar en el que ocurrirá, pero sabemos que sigue una distribución de Poisson. Esta distribución describe eventos raros o infrecuentes que ocurren de forma aleatoria e independiente[34, 35]. Así pues, la probabilidad P de que aparezcan m núcleos supercríticos en un intervalo de tiempo determinado τ y que sigue una distribución de Poisson, está determinada por:

$$P(m, \tau) = \frac{(\lambda \tau)^m \exp(-\lambda \tau)}{m!} \quad (4.68)$$

donde λ representa el número medio de eventos por unidad de tiempo. Es una constante que para valores fijos de presión y temperatura coincide con la densidad de probabilidad de formación de un núcleo crítico, es decir coincide con la tasa de nucleación por el volumen del sistema ($\lambda = JV$). Si no estuviéramos en un estado estacionario este parámetro dependería del tiempo, aparte de poder depender de la temperatura y la presión, pero en estos casos el evento de nucleación no se ajustaría a una distribución de Poisson, y en esta tesis no se va a tratar dicho caso.

Partiendo de la ecuación 4.68, la probabilidad de que no suceda ningún evento ($m = 0$) en un intervalo de tiempo τ es:

$$P(0, \tau) = \exp(-\lambda \tau). \quad (4.69)$$

Cuando nos encontramos en condiciones de alta metaestabilidad en el sistema, como sería una alta supersaturación (ver capítulo 7), el tiempo que tarda en aparecer un núcleo es mucho mayor que el que tarda en crecer. Por tanto para que ocurra una transición de fase en todo el sistema es suficiente con que aparezca un único núcleo. Por otro lado la nucleación es un evento considerado raro porque suele tomar largos tiempos de simulación para que se produzca (la probabilidad de que aparezca un núcleo es baja en los tiempos y tamaños de sistema estándar de simulación). Aun así cuando hacemos simulaciones del sistema para observar cuándo ocurre espontáneamente la nucleación la ventana de condiciones en la que podemos llevar a cabo el estudio observándose un único evento es pequeña (normalmente se quiere evitar tratar con varios eventos consecutivos, como es el caso de esta tesis). Esta condición en la que únicamente ocurre un evento por simulación se cumple mejor cuanto más pequeño sea el sistema (menor V). En este caso, en el que solo se produce un evento de nucleación por simulación, solo nos interesará caracterizar el tiempo que tarda en ocurrir un evento.

La probabilidad de que suceda al menos un evento en un intervalo de tiempo τ es 1 menos la probabilidad de que no suceda ningún evento:

$$P(m \geq 1, \tau) = 1 - \exp(-\lambda \tau). \quad (4.70)$$

La densidad de probabilidad de que suceda al menos un evento por unidad de tiempo, t , es la derivada con respecto al tiempo de la expresión anterior:

$$\omega(m \geq 1, t) = \lambda \exp(-\lambda t). \quad (4.71)$$

El primer momento de esta función de distribución de probabilidad es el tiempo promedio en el que sucede el primer evento, $\langle t \rangle$. ω es una función continua, por ello, para obtener $\langle t \rangle$, debemos multiplicarla por el tiempo e integrarla en todo el rango de probabilidades de tiempo:

$$\langle t \rangle = \int_0^\infty t \omega(t) dt = \int_0^\infty \lambda t \exp(-\lambda t) dt = \lambda^{-1}. \quad (4.72)$$

Cuando hacemos simulaciones lo que obtenemos es t_i , el tiempo que ha tardado en aparecer un núcleo crítico en la simulación i . Para poder usar directamente estos datos expresamos como obtener el tiempo promedio en el que se produce un evento de nucleación de manera discreta:

$$\langle t \rangle = \sum_{i=1}^n \frac{t_i}{n}. \quad (4.73)$$

Finalmente podríamos calcular la tasa de nucleación J de nuestro set de simulaciones, teniendo en cuenta que se refiere al número de clusters críticos por unidad de tiempo y volumen [36, 35, 37].

$$J = \frac{1}{V} \frac{\partial m(t)}{\partial t}. \quad (4.74)$$

Así podemos expresar el número de clusters críticos como:

$$m(t) = \int_0^t J V dt. \quad (4.75)$$

Si el tiempo que usamos es $\langle t \rangle$, es decir el tiempo que tarda en formarse el primer clúster $m = 1$ tenemos que:

$$1 = \int_0^{\langle t \rangle} J V dt. \quad (4.76)$$

Y como J es constante podemos escribir:

$$J = \frac{1}{V \langle t \rangle}. \quad (4.77)$$

Expresión que también se recupera combinando la igualdad de la ecuación 4.72 $\langle t \rangle = \lambda^{-1}$ con la definición para la el número medio de eventos por unidad de

tiempo $\lambda = JV$. La ecuación 4.77 nos muestra que la tasa de nucleación depende del tiempo promedio para que ocurra la nucleación y del volumen del sistema. Cuando el tiempo promedio para que ocurra la nucleación disminuye (es decir, la nucleación ocurre más rápidamente), la tasa de nucleación aumenta. Además, cuanto mayor sea el volumen del sistema, mayor será el número de eventos de nucleación, ya que habrá más espacio para la formación de núcleos, aunque la tasa de nucleación J sera invariante al tamaño del sistema.

Con todas las expresiones vistas hasta ahora queda cubierto el cómo calculamos la tasa de nucleación en los distintos casos estudiados. A continuación se explican los distintos modelos de potencial utilizados en esta tesis.

4.3 Modelos de simulación

En la presente sección, describimos los modelos de potencial que se han empleado en las simulaciones. Cabe destacar que el modelo de potencial, también denominado campo de fuerza, juega un papel esencial en la simulación del sistema, puesto que la capacidad de reproducir los resultados experimentales depende de la bondad del potencial. Se comienza presentando el modelo con interacciones más sencillas de los que se ha estudiado en esta tesis. Este es el modelo Lennard-Jones, ya que en contraposición con el resto de modelos estudiados, no presenta cargas (no hay potencial Coulómbico).

4.3.1 Lennard-Jones

En el capítulo 9 cuyo objetivo es adaptar la metodología de *Seeding NVT* para mezclas, se necesita un potencial sencillo y rápido de simular. El modelo más sencillo con transición líquido-vapor es el potencial de Lennard-Jones (LJ) [38]. Este potencial puede ser utilizado para representar de forma realista los gases nobles. Las partículas interactúan entre sí debido a dos factores: la repulsión y la atracción. Estas fuerzas son descritas matemáticamente usando la siguiente ecuación de potencial:

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (4.78)$$

donde r es la distancia entre dos partículas, ϵ es la profundidad del pozo de potencial (energía de interacción) y σ es la distancia a la cual el potencial se anula. El modelo supone que la energía de interacción aumenta bruscamente cuando las partículas se acercan demasiado entre sí, es decir, cuando comienzan a repelerse entre sí. Es común encontrarlo como parte de un campo de fuerza más complejo como son los de agua que explicaremos a continuación.

A pesar de su simplicidad, la implementación del potencial en cuestión en simulaciones de dinámica molecular se presenta como un desafío debido a la necesidad de truncar este potencial continuo y de alcance infinito, impidiendo su

derivación. Para superar esta dificultad, el potencial se desplaza en el eje vertical en conjunto con su derivada, de tal forma que ambos se anulan de manera continua cuando el radio se acerca a un valor predefinido, $r_c = 2,5\sigma$. Como resultado, se obtiene un nuevo potencial, conocido como TSF-LJ [39], truncado y desplazado en su derivada. Este potencial es el que usamos en el capítulo 9 y sigue la ecuación:

$$U_{TSF-LJ}(r) = U_{LJ}(r) - U_{LJ}(r_c) - (r - r_c)U'_{LJ}(r_c) \quad (4.79)$$

en la que $U_{LJ}(r_c)$ se refiere al valor del potencial Lennard-Jones en $r = r_c$ y $U'_{LJ}(r_c)$ al valor de la derivada del potencial en $U'_{LJ}(r_c)$.

A continuación se detallan los modelos de agua utilizados comenzando con el modelo de agua TIP4P/2005.

4.3.2 Agua TIP4P/2005

El modelo de agua TIP4P/2005[40] es uno de los modelos más utilizados en simulación de agua y el que usamos en el capítulo 8 para estudiar la formación de burbujas o cavitación en agua. Este modelo representa el agua como una molécula rígida, compuesta por cuatro sitios de interacción. La posición del oxígeno (O) es el sitio con interacción Lennard-Jones. Los sitios con cargas puntuales son los hidrógenos (H), y el cuarto sitio, llamado sitio M, se coloca en el bisector del ángulo H-O-H y es coplanar con los sitios O y H. Así pues, el potencial aparte de ser aditivo por pares, tiene dos contribuciones, una de tipo Lennard-Jones (Van der Waals) y otra Coulombica (electrostática).

Es importante destacar que la distancia O-H y el ángulo H-O-H son fijos e iguales a los valores experimentales, que son de 0,09572 nm y 104,52°, respectivamente. En la figura 4.2 se muestra esquemáticamente una molécula según este modelo.

La energía potencial Lennard-Jones viene dada por la ecuación:

$$U_{LJ}^{OO} = 4\epsilon \left[\left(\frac{\sigma}{r_{OO}} \right)^{12} - \left(\frac{\sigma}{r_{OO}} \right)^6 \right] \quad (4.80)$$

donde r_{OO} es la distancia entre los oxígenos de las dos moléculas que interactúan y ϵ es la profundidad del pozo de potencial (energía de interacción). Además la energía electrostática entre un par de moléculas a y b viene dada por la siguiente ecuación:

$$U_{Coulomb} = \frac{e^2}{4\pi\epsilon_0} \sum_{a,b} \frac{q_a q_b}{r_{ab}} \quad (4.81)$$

donde e es la carga del protón, ϵ_0 es la permitividad en el vacío, q_a es la carga del sitio de interacción a y q_b es la carga del sitio de interacción b . q_a y q_b

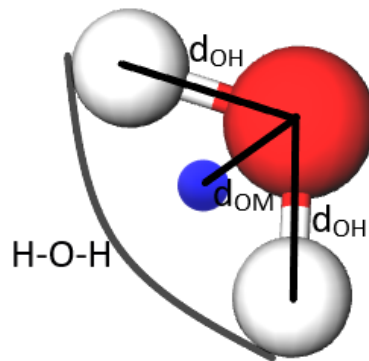


Figura 4.2. Esquema de una molécula de agua según el modelo TIP4P/2005. En rojo tenemos el oxígeno, en blanco los dos hidrógenos y en azul el sitio M.

se presentan en unidades de la carga del electrón, e , de tal modo que son adimensionales. Cabe recordar que al término electrostático contribuyen únicamente los sitios H y M.

Así pues este potencial está definido por cuatro parámetros: La profundidad del pozo de potencial ϵ , el tamaño del centro Lennard-Jones σ , la carga del sitio H q_H y la distancia d_{OM} entre el oxígeno y el sitio M. No hemos mencionado la carga del sitio M porque se relaciona con la del sitio H de forma sencilla, $q_H = -q_M/2$. Los parámetros que corresponden con el modelo TIP4P/2005 son: $\epsilon/k = 93,2$ K, $\sigma = 0,31589$ nm, $q_H = 0,5564$ e y $d_{OM} = 0,01546$ nm.

En la figura 4.3 se muestra el diagrama de fases del modelo, que indica cuál es la fase estable a distintas condiciones de presión y temperatura. Este diagrama es bastante similar al experimental en términos cualitativos y casi idéntico en términos cuantitativos. Es importante destacar que el modelo es capaz de reproducir el máximo de densidad del agua a una temperatura de 4°C , a pesar de que su punto de fusión a presión ambiente es de 250 K.

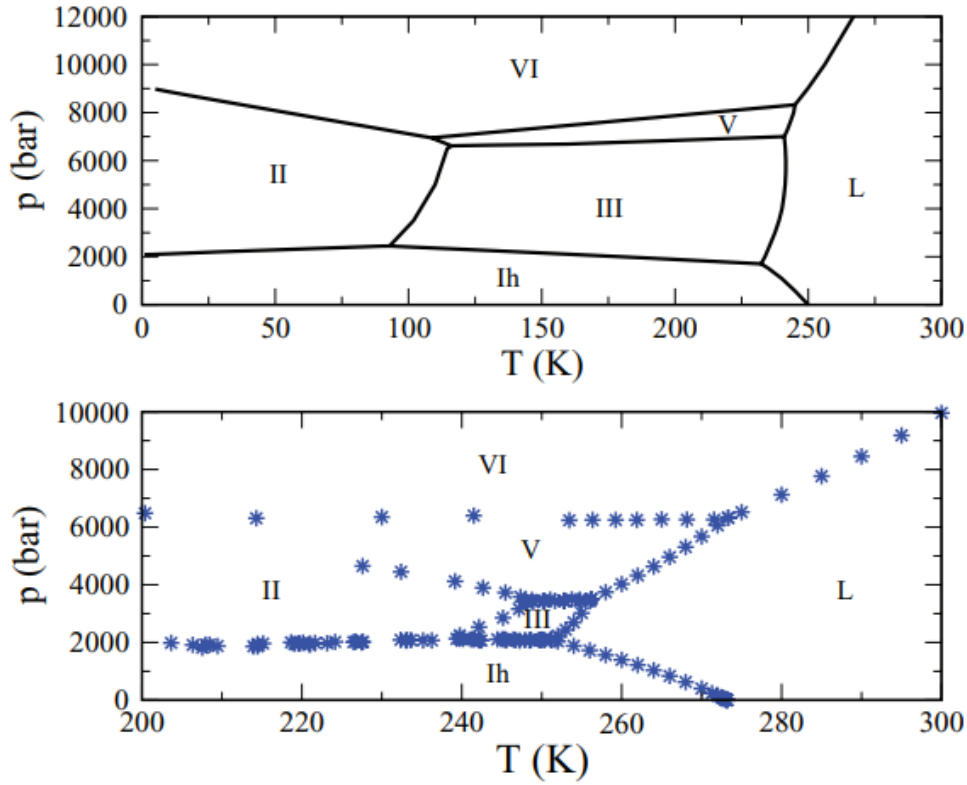


Figura 4.3. Diagrama de fases del agua que muestra los resultados obtenidos por la simulación del modelo TIP4P/2005 en el panel de arriba y los experimentales en el de abajo. La imagen ha sido obtenida de la Ref. [41].

4.3.3 Agua SPC/E

Es un modelo de agua rígido no polarizable con tres sitios de interacción presentado en 1987 por Berendsen *et al.* [42]. Su nombre en inglés es *extended simple point charge model*, de aquí vienen las siglas SPC/E. El potencial por pares viene descrito por un término LJ y uno Coulombico. La distancia entre el oxígeno y los hidrógenos es de 0,1 nm, las cargas puntuales se sitúan en el oxígeno y los hidrógenos y el ángulo HOH es igual al ángulo tetraédrico ($109,47^\circ$). La interacción LJ entre pares de oxígenos viene dada por la misma ecuación Eq. (4.80) que hemos visto para otros modelos simulando las fuerzas Van der Waals y la Coulombica por la ecuación Eq. (4.81) que también vimos para el anterior modelo de agua. En este caso los parámetros son $\varepsilon = 0,6502 \text{ kJ mol}^{-1}$, $\sigma = 0,31656 \text{ nm}$, $q_H = 0,4238 e$ y para cumplir la electroneutralidad de carga $q_O = -q_H \times 2$.

En la figura 4.4 se muestra el diagrama de fases del modelo. Reproduce peor los experimentos que el modelo TIP4P/2005 (comparar con la figura 4.3), siendo su punto de fusión del hielo I_h a presión ambiente de 215 K. De todos modos es un modelo más antiguo y se sigue usando mucho, por lo que tiene elevada relevancia

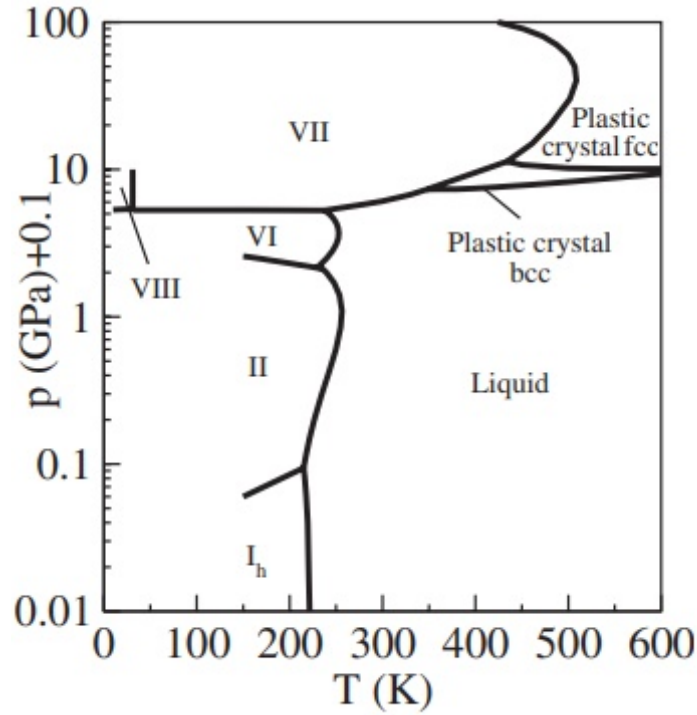


Figura 4.4. Diagrama de fases para el agua SPC/E [43].

en el panorama actual.

4.3.4 Agua-NaCl JC/SPC/E

En 2008 se parametrizó un potencial para simular el agua SPC/E que acabamos de describir junto con sal común (cloruro sódico, NaCl) [44]. Para los iones se usa la carga experimental de $+1 e$ y $-1 e$. Se simulan las interacciones Coulombicas entre los iones y el agua con la ecuación 4.81, que ya vimos con anterioridad. Por otro lado para las interacciones LJ ion-agua se sigue la ecuación 4.78, aplicando las reglas de combinación de Lorentz-Berthelot [45, 46]:

$$\begin{aligned}\sigma_{ab} &= \frac{\sigma_{aa}\sigma_{bb}}{2} \\ \epsilon &= \sqrt{\epsilon_{aa}\epsilon_{bb}}\end{aligned}\tag{4.82}$$

Los parámetros para el cloruro, Cl^- , son $\epsilon = 0,053493 \text{ kJ mol}^{-1}$, $\sigma = 4,830 \text{ nm}$, y para el sodio Na^+ , son $\epsilon = 1,475465 \text{ kJ mol}^{-1}$, $\sigma = 2,159 \text{ nm}$.

La solubilidad para este modelo se ha estudiado mucho hasta llegar a un valor consensuado de $3,7 \text{ mol kg}^{-1}$ [47, 48, 49, 50] a 1 bar y 298,15 K. Este valor se encuentra bastante por debajo del experimental $6,15 \text{ mol kg}^{-1}$, pero durante un tiempo fue el mejor modelo disponible y por ello se extendió su uso. En el capítulo

7 se usa este modelo porque había cálculos previos para la tasa de nucleación de la sal hechos con este modelo para distintos métodos al que nosotros empleábamos y nos permitía validar nuestro método. También se usa este potencial en el capítulo 5 para obtener el diagrama de fases agua-NaCl, pero combinándolo con el modelo TIP4P/2005 [40] para el agua y usando las reglas de Lorentz-Berthelot para la interacción entre los iones y el agua.

4.3.5 Agua-sales Madrid-2019

El modelo Madrid-2019 se desarrolló como su nombre indica en 2019, en el grupo de investigación madrileño en el que he desarrollado mi Tesis [51]. Este modelo usa para el agua el potencial TIP4P/2005 desarrollado por el mismo grupo [40].

El contexto en el que surge la necesidad de desarrollar un nuevo modelo para sales es el siguiente. La mayoría de los modelos de disoluciones salinas acuosas predicen una solubilidad bastante baja comparada con la experimental [52, 53, 54, 55, 56]. Además debido a la baja solubilidad del campo de fuerza, se observa que la formación de pares iónicos y la precipitación en disoluciones es demasiado alta [57, 58, 59, 60]. Por otro lado se ha observado que los campos de fuerza comunes sobreestiman el aumento de la viscosidad debido a la adición de sal en comparación con los experimentos [61, 51]. También se ha señalado que la mayoría de los potenciales (incluyendo los polarizables) producen una disminución mayor en el coeficiente de difusión que la experimental [62]. Para remediar esta situación, se ha propuesto el uso de cargas escaladas para los iones, lo que mejora la descripción del coeficiente de difusión del agua en soluciones iónicas [63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75].

En el modelo Madrid-2019, se usan por tanto cargas escaladas para representar la polarización efectiva en disolución [51]. Este enfoque ha demostrado mejorar la descripción de la viscosidad, del coeficiente de difusión del agua, de los coeficientes de actividad y de las solubilidades. En contrapartida, su uso empeora la predicción de las energías libres de hidratación y no se recomienda para sales fundidas o para la fase sólida [76, 77, 78].

Una vez más hay interacciones LJ y Coulombicas entre iones y agua y por tanto las ecuaciones que las describen son las ecuaciones 4.78 y 4.81. Las cargas usadas son de $0,85\,e$ para iones monovalentes y $1,7\,e$ para divalentes, estos valores permiten recuperar la ley de Debye-Huckel correcta compensando las deficiencias de la constante dieléctrica del agua TIP4P/2005 [66]. En las simulaciones se usó el archivo *topol.top* que se proporciona en el material suplementario de la Ref. [51], ahí se compilan los distintos parámetros ϵ y σ para las distintas sales del modelo y el agua TIP4P/2005. Los iones descritos por este modelo son: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- y SO_4^{2-} .

El modelo Madrid-2019 se usa en el capítulo 6 para estimar el descenso crioscópico de distintas disoluciones salinas. Aunque en esta tesis no se tratan sales con otros iones cabe mencionar que en los últimos años se ha ido ampliando el modelo para otras sales [79].

4. Fundamento teórico

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Phase diagram of the NaCl-water system from computer simulations

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5.1 Abstract

NaCl aqueous solutions are ubiquitous. They can crystallize into ice, NaCl or NaCl·2H₂O depending on the temperature-concentration conditions. These crystallization transitions have important implications in geology, cryopreservation or atmospheric science. Computer simulations can help understand the crystallization of these solids, which requires a detailed knowledge of the equilibrium phase diagram. We use molecular simulations in which we put at contact the solution with the solid of interest to determine points of the solid-solution coexistence lines. We follow two different approaches, one in which we narrow down the melting temperature for a given concentration, and another one in which we equilibrate the concentration for a given temperature, obtaining consistent results. The phase diagram thus calculated for the selected model (TIP4P/2005 for water molecules and Joung-Cheatham for the ions) correctly predicts coexistence between the solution and ice. We were only able to determine NaCl·2H₂O-solution coexistence points at higher temperatures and concentrations than in the experiment, so we could not establish a direct comparison in this case. On the other hand, the model underestimates the concentration of the solution in equilibrium with the NaCl solid. Our results, alongside other literature evidence, seem to indicate that

ion-ion interactions are too strong in the model. Our work is a good starting point for the improvement of the potential model and for the study of the nucleation kinetics of the solid phases involved in the phase diagram.

5.2 Introduction

The presence of saline aqueous solutions is ubiquitous, ranging from sea water to sea-spray clouds [1, 2] or physiological solutions. The most abundant salt of them all is sodium chloride (NaCl), being the phase behaviour of water-NaCl mixtures of great interest [3, 4]. An NaCl aqueous solution (known as brine) transforms into ice when cooled at low-moderate salt concentration [5]. When the solution is supersaturated above $\sim 0^\circ\text{C}$, solid NaCl (rock salt), precipitates [6], whereas a solid containing both NaCl and water, $\text{NaCl}\cdot 2\text{H}_2\text{O}$, known as hydrohalite, forms when cooling a concentrated brine [4, 7].

The phase transitions above mentioned have great implications on atmospheric science [3], geology [8, 9] or cryopreservation [10, 11]. Therefore, understanding the thermodynamic and kinetic factors controlling them is very important.

On the experimental side, the thermodynamic phase diagram of water-NaCl mixtures is already well known [12, 13, 14, 4]. The study of the kinetics of phase transitions, on the contrary, poses a great challenge and there is still an intense research activity devoted to investigate the onset of ice [15, 16, 5], NaCl [6, 17, 18] and $\text{NaCl}\cdot 2\text{H}_2\text{O}$ [4, 7] crystallization from the brine.

Computer molecular simulation is a very suitable tool for the study of crystal nucleation because it has access to the nanoscopic scale, which is the relevant one for the understanding of the initiation of crystallization [19, 20]. Using this research tool, there are studies of ice nucleation from salty water [15, 21, 22, 23, 24] and of rock salt precipitation from a supersaturated brine [24, 25, 26, 27, 28, 29, 30]. There are also simulation studies of the NaCl-solution [31, 32] and of the ice-solution interfaces [33, 34, 35].

These simulation studies that closely look at crystal nucleation or at the solid-solution interface require a well-known equilibrium phase diagram of the selected interaction potential in order to control the thermodynamic drive for the emergence of the solid phase. However, computing the location of the borders between the different phases involved is not an easy task. For instance, many years have been required in order to reach a consensus in the calculation of the coexistence between rock salt and the solution for just a single temperature [36, 37, 38, 39, 40, 41, 42, 43, 44, 32]. Moreover, little is known of the ability of the existing model potentials to reproduce the whole ice-solution coexistence line [21, 23, 35] and, to the best of our knowledge, no one has attempted so far to calculate a single coexistence point between the brine and hydrohalite.

In this work we try to fill this gap and compute the coexistence lines between the solution and the three solid phases involved –ice, rock salt and hydrohalite– for a given interaction potential. To obtain coexistence points we perform direct

coexistence molecular dynamic simulations where the phases involved are put in contact. The agreement between the computed and the experimental coexistence lines with the brine is quite good for ice. The hydrolite-solution line of the model has the same slope as the experimental one, but appears at higher concentrations and temperatures. Finally, the solubility of NaCl is underestimated by the model.

The computed phase diagram is a good starting point for simulation studies of crystal nucleation, of the dynamics of aqueous NaCl solutions, of the solid-solution interface, as well as for works aiming at improving the interaction potential describing the NaCl-water system.

5.3 Methods

5.3.1 Model potentials

We use the TIP4P/2005 model to describe the interaction between water molecules [45] and the Joung Cheetham (JC) potential parametrized for SPC/E water to account for ion-ion interactions [46]. The ion charge interacts with the charges of the water molecule with the Coulomb law, while the ion-water Lennard Jones interaction obeys the Lorentz-Berthelot [47, 48] combination rules. The cut-off radius for the neighbor list, Lennard Jones and coulombic interactions has been set to 9 Å. Standard long range corrections are added to the calculation of Lennard Jones interactions. This is not strictly rigorous for heterogeneous systems. However, the density difference between the coexisting phases is not large. Moreover, we have checked for some specific cases that switching the Lennard-Jones interaction off between 12 and 13 Å and not including long range corrections gives the same results. Long range coulombic interactions are dealt with the smooth particle mesh Ewald method.

This potential to simulate NaCl/H₂O systems has been previously employed in studies of ice nucleation from salty water [21, 22] and in a study where the solubility of the NaCl salt in water was determined to be 3,49 mol kg⁻¹ at 298 K [38]

5.3.2 Simulation details

Simulations are performed with GROMACS in the NpT ensemble, fixing the pressure to $p = 1$ bar and adopting an integration time step of 2 fs. The pressure applies anisotropically along the XYZ dimensions to accommodate the crystal structure. We use the Nose-Hoover thermostat, with a relaxation time of 1 ps, and the Parrinello-Rahman barostat with a relaxation time of 2 ps.

5.3.3 Phase diagram

The phases involved in the phase diagram are the liquid—an NaCl aqueous solution—and three solids: ice Ih, NaCl rock salt and the dihydrated NaCl solid, $\text{NaCl}\cdot 2\text{H}_2\text{O}$. In the temperature-composition plane at 1 bar, shown in Fig. 5.1, there are three coexistence lines: ice-solution (blue in Fig. 5.1), $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution (magenta) and NaCl-solution (orange). We use molality, m , or moles of NaCl per kg of water, as concentration unit. Solid curves correspond to the experimental phase diagram and symbols to simulation data (solid ones from this work and empty ones from previous papers as indicated in the figure caption). In order to compare experiments and simulations, temperature has been scaled by the ice melting temperature (273,15 K for the experiment and 250 K for the model [49, 50]). Fig. 5.1 is the main result of this work and will be discussed in more detail later on.

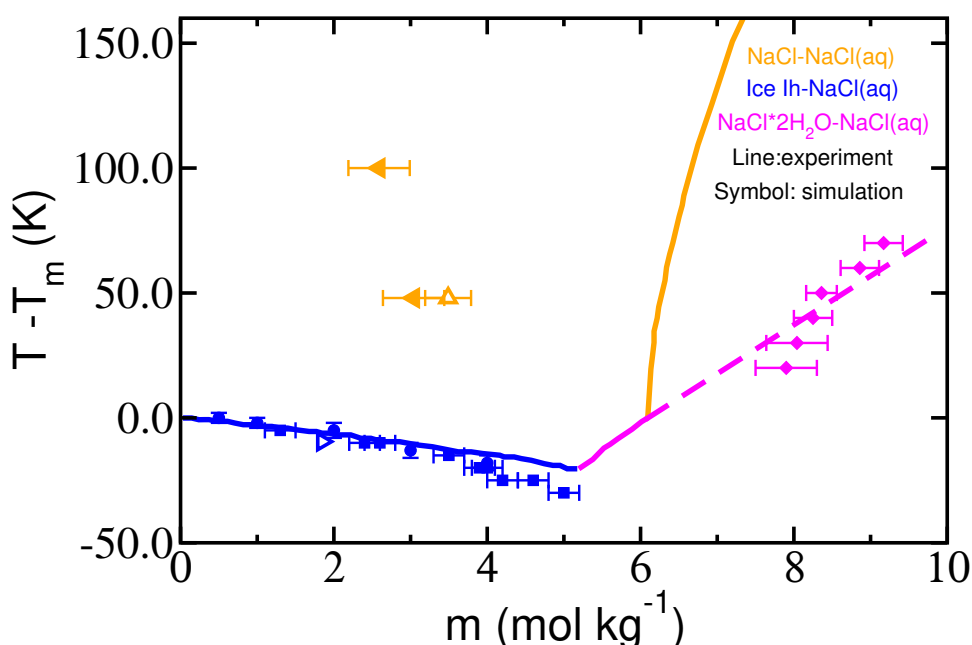


Figure 5.1. Phase diagram of the NaCl/water system in the temperature-concentration plane at 1 bar. Temperature is given relative to the melting point of pure water, which is 250 K for the model [49, 50]. The high-temperature low-concentration area of the phase diagram corresponds to the NaCl aqueous solution (NaCl(aq)). The coexistence between NaCl(aq) and ice Ih, NaCl and NaCl·2H₂O is shown in blue, orange and magenta respectively. Solid curves correspond to experimental coexistence lines whereas symbols correspond to simulation data. The dashed magenta curve is a linear extrapolation of the experimental NaCl(aq)-NaCl·2H₂O line. Filled symbols correspond to this work, whereas the blue empty one has been taken from Ref. [21] and the orange empty one from Ref. [38].

5.3.4 Direct Coexistence

The simulation points in Fig. 5.1 have been computed with the Direct Coexistence method [51], which consists in simulating a solid and a fluid in contact. In Fig. 5.2, we show typical initial configurations corresponding to the study of the coexistence lines mentioned in the previous paragraph.

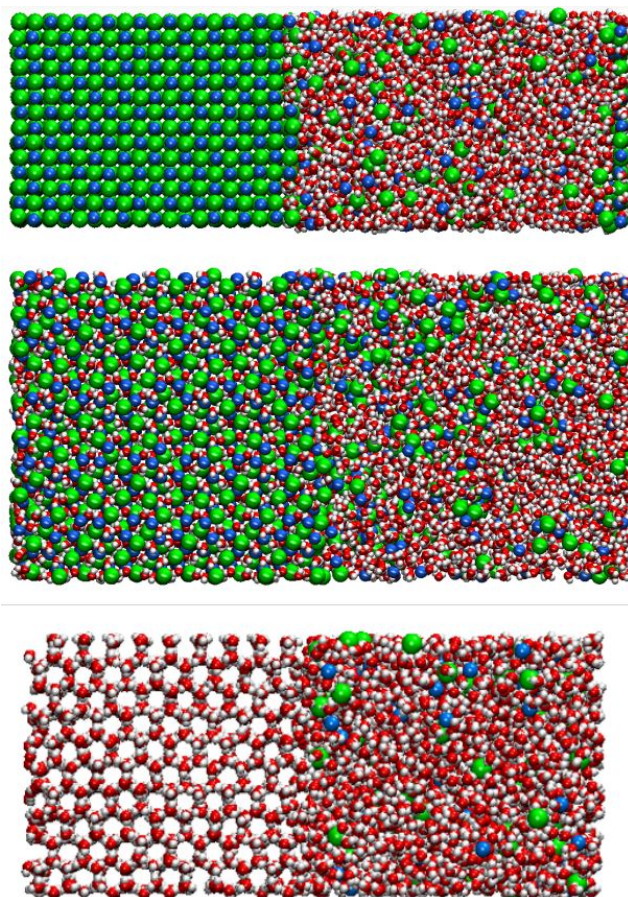


Figura 5.2. Snapshots of typical initial configurations used in the direct coexistence runs to obtain coexistence points along the NaCl-solution (top), NaCl·2H₂O-solution (middle) and the ice-solution (bottom) lines of the phase diagram. Green and blue spheres correspond to Na⁺ and Cl⁻ ions respectively whereas red and white ones represent oxygen and hydrogen atoms of the water molecule.

Keeping this in mind there are two strategies to determine coexistence in a mixture:

Narrow down Direct Coexistence (NdDC)

This is the most widely used version of Direct Coexistence [52, 53, 54]. In this scheme one of the two phases that are put in contact grows at the expense of the other. In our case, if the simulation temperature is higher than the melting

5. Phase diagram of the NaCl-water system from computer simulations

temperature for the imposed pressure and concentration the solid slab melts, and vice versa. In this case the melting temperature is narrowed down in between the highest temperature for which the solid grows and the lowest for which it melts. Analogously, the coexistence pressure can be narrowed down by keeping the temperature constant and performing simulations at different pressures [52, 54]. This method is sketched in Fig. 5.3. In the middle, we show a snapshot of the starting configuration in which ice Ih is placed at contact with a 2 mol kg^{-1} NaCl solution. The liquid slab is much larger than the solid one in order to minimize concentration changes during the simulation. When the system is simulated at 1 bar and 248 K the solid melts (top snapshot), whereas it grows at 235 K (bottom snapshot). In view of these simulations, the coexistence temperature between ice and a 2 mol kg^{-1} NaCl solution can be narrowed down to $(241,5 \pm 6,5) \text{ K}$. We note that in the final configuration at 235 K, shown in Fig. 5.3, a few ions are found doping the ice structure in agreement with previous studies on ice doping for this type of potential models [34, 55]. We have already used the NdDC method to determine coexistence in mixtures [21].

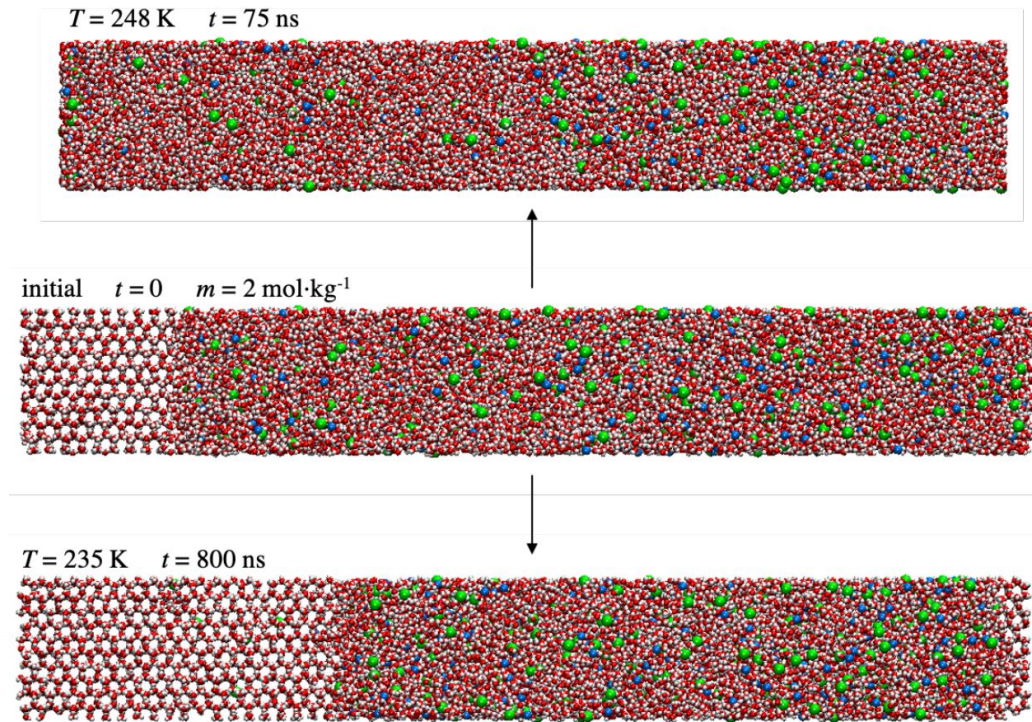


Figure 5.3. Sketch of the NdDC method. In the middle, an initial configuration of ice Ih in contact with a 2 mol kg^{-1} NaCl solution. Top (bottom), final configuration after a simulation at 248 K (235 K).

In this work, we have used the NdDC method for the ice-solution coexistence. We have chosen five different initial molar concentrations of the NaCl(aq) phase ranging from $0,5 \text{ mol kg}^{-1}$ to 4 mol kg^{-1} . The system sizes are $L_x \approx 29 \text{ nm}$, $L_y \approx 3,9 \text{ nm}$, and $L_z \approx 3,7 \text{ nm}$. The solid-liquid phases are in contact along the

$Y - Z$ plane, and the X size of the crystal is $\approx 4,5$ nm. In all our ice-solution direct coexistence simulations the secondary prism ice face is exposed to the liquid, which is the fastest face to grow [56].

Equilibrium Direct Coexistence (EDC)

The NdDC method is the only possibility for monocomponent systems at constant pressure. In this work, we deal with a mixture and, thereby, composition is another thermodynamic variable. Since the system is finite, as the solid grows or melts the concentration in the fluid part of the system changes accordingly. Therefore, the coexistence composition can be spontaneously equilibrated by simulating long times. Such EDC strategy has already been used to obtain coexistence points between NaCl(aq) and the NaCl solid [43, 37, 57, 58] and between ice and salty water [23]. The method is illustrated in Fig. 5.4. On the left, we show an initial configuration where ice is put in contact with a 2 mol kg^{-1} NaCl aqueous solution. From such initial configuration, $1 \mu\text{s}$ simulations were performed at three different temperatures, 240, 235 and 230 K. The final configuration for each temperature is shown on the right hand side of the figure. It can be clearly seen how ice grows in all cases from the initial configuration. It is also evident that the lower the temperature the wider the ice slab and, consequently, the higher the concentration in the adjacent solution. This is consistent with the fact that the ice Ih-solution line in the phase diagram has a negative slope.

These are the employed system sizes with the EDC method: For ice Ih in contact with the solution the box sides are $L_x \approx 9$ nm, $L_y \approx 3,9$ nm, and $L_z \approx 3,7$ nm. The solid-liquid phases are in contact along the $Y - Z$ plane, and the X size of the crystal is $\approx 4,5$ nm. The set up of the initial configuration is similar to that of the NdDC method with the difference that now the size of the solution is noticeably smaller reducing the computation time. The ice pII plane is exposed to the solution.

The sizes of the simulation box for the NaCl crystal in contact with the solution are $L_x \approx 11,8$ nm, $L_y \approx 4,05$ nm and $L_z \approx 4,05$ nm. Solid and liquid phases are placed at contact along the $Y - Z$ plane. The X size of the crystal is ≈ 5 nm. Some simulations have been repeated increasing the system size up to $L_y \approx 4,65$ nm and $L_z \approx 4,65$ nm. The crystal layer in contact with the solution cannot be completely flat because that makes the kinetics of attachment detachment of ions too slow [37]. To avoid this problem, we randomly remove some ions from the outmost layer while keeping global electroneutrality. We have exposed the (100), (110) and (111) planes to the solution.

The sizes of the simulation box for the NaCl·2H₂O crystal in contact with the solution are $L_x \approx 3,8$ nm, $L_y \approx 12,3$ nm, and $L_z \approx 6,0$ nm. The solid-liquid phases are in contact along the $X - Z$ plane, and the Y size of the crystal is $\approx 5,7$ nm. The crystal plane exposed to the solution is (010).

5. Phase diagram of the NaCl-water system from computer simulations

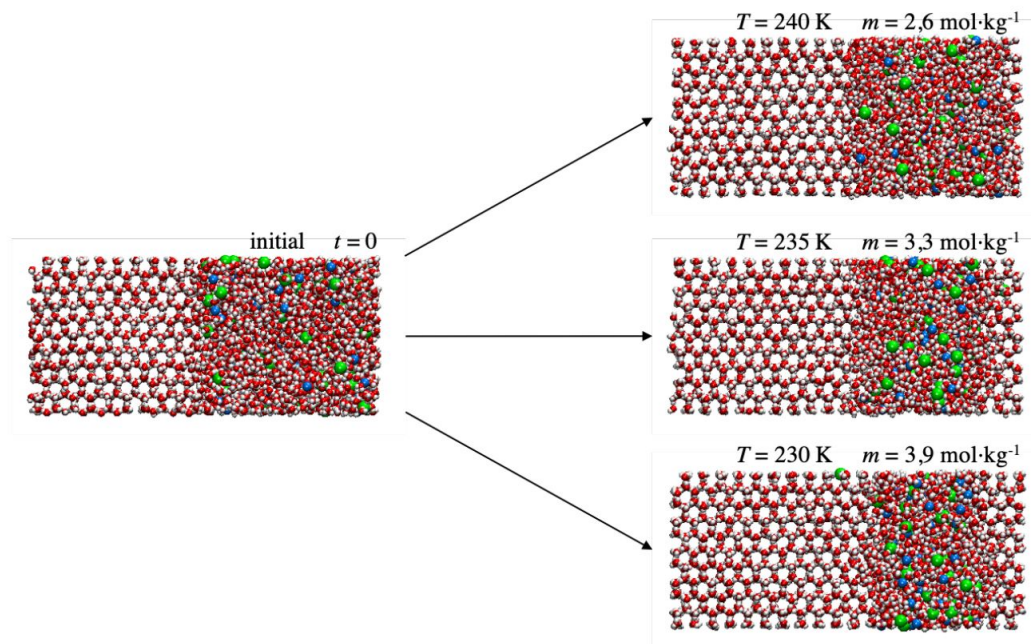


Figura 5.4. The EDC method applied to the equilibrium between ice Ih and the NaCl solution. Left: initial configuration where the solid is put at contact with a $\approx 2 \text{ mol kg}^{-1}$ solution. Right: final configurations for 1 μs runs at 240 K (top), 235 K (middle) and 225 K (bottom). For a given pressure and temperature the system finds by itself the equilibrium concentration. In this example, ice growth from the starting configuration is larger the lower the temperature and, consequently, the concentration of the solution increases when temperature decreases.

5.3.5 Calculation of the concentration

The concentration is calculated by performing density profiles of water and NaCl along the coordinate perpendicular to the interface. We use the GROMACS tool *gmx density* for that purpose. We compute the density along the perpendicular direction to the interface averaged over 20 ns. In Fig. 5.5 we give an example of such density profiles for the three types of coexistence studied. The oscillating part of the density profile corresponds to the solid slab whereas the flat one does correspond to the solution. From the average values of the water and NaCl densities in the solution, ρ_w and ρ_{NaCl} , and the molar mass of NaCl, $M_{NaCl} = 0,05844 \text{ kg mol}^{-1}$, we compute the concentration as:

$$m = \frac{\rho_{NaCl}}{\rho_w \times M_{NaCl}} \quad (5.1)$$

where the densities are given, as in Fig. 5.5, in kg m^{-3} . To compute the densities ρ_{NaCl} and ρ_w we use a solution slab away from the solid-solution interface indicated by the dashed vertical lines in Fig. 5.5.

5.4 Results

5.4.1 NaCl·2H₂O

The bulk thermodynamic and dynamic properties of the selected model have been widely investigated by computer simulations for all phases involved [45, 46, 43, 59, 38, 21, 22, 60] except for the NaCl·2H₂O solid, for which there are not many simulation studies. The atomic coordinates of NaCl·2H₂O were obtained from the Inorganic Crystal Structure Database [61, 62]. Simulations of this crystal have already been performed using a polarizable force field [63, 64], finding a reasonable agreement between simulated and experimental unit cell parameters at $T = 150 \text{ K}$. In Fig. 5.6 we compare the NaCl·2H₂O experimental equation of state with the model prediction, which is quite accurate, giving a unit cell volume only about 2 percent higher than the experimental one. Fig. 5.6 also shows that the model we use and the polarizable one used in Refs. [63, 64] give a very similar unit cell volume.

5. Phase diagram of the NaCl-water system from computer simulations

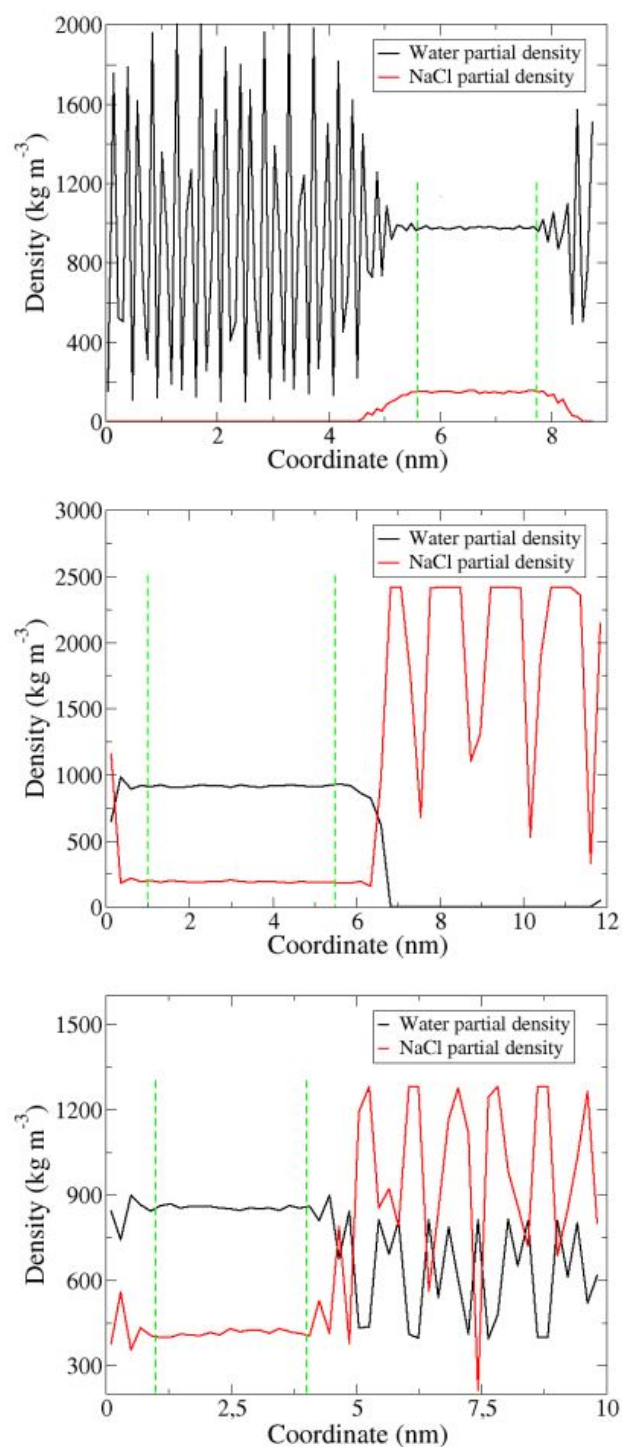


Figura 5.5. Density profiles along the direction perpendicular to the interface for NaCl and water in three of the EDC simulations. Top, ice-NaCl(aq) system at 240 K. Middle, NaCl-NaCl(aq) system at 355 K. Bottom, NaCl·2H₂O-NaCl(aq) system at 290 K. The region used to calculate the concentration is comprised between the 2 vertical green dashed lines.

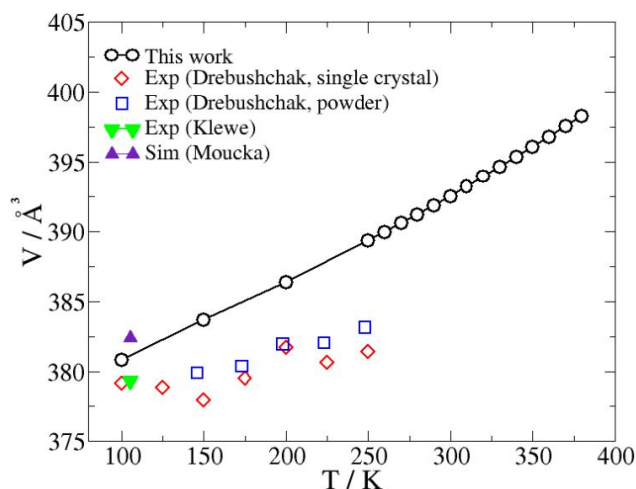


Figura 5.6. Unit cell volume of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ as obtained in simulations and from x-ray experiments using single-crystal and powder diffraction samples[65].

5.4.2 NdDC

We have used this method for the ice-solution equilibrium. In Fig. 5.7 we give an example of the way we narrow down coexistence for ice in contact with a 2 kg mol^{-1} NaCl solution. We perform runs starting from a given configuration at different temperatures and monitor the potential energy. If ice grows the potential energy goes down and vice versa. In this way we narrow the coexistence temperature for this concentration down to $(243,5 \pm 1,5) \text{ K}$. The system employed is large enough to ensure that concentration does not change more than 1-2 % during the runs. In addition, these runs do not need to be as long as EDC ones because one is not interested in equilibrating the concentration, but rather in determining whether for a given concentration ice grows or melts. The results obtained with the NdDC method are reported in table 5.1 and plotted as blue circles in Fig. 5.1.

5. Phase diagram of the NaCl-water system from computer simulations

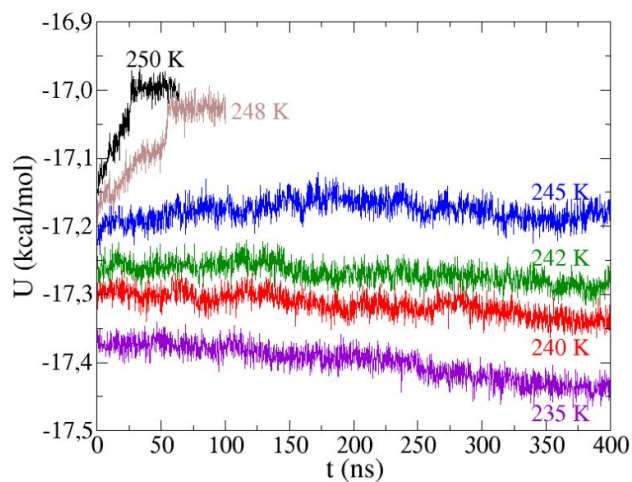


Figura 5.7. Example of the application of the NdDC method to the coexistence between ice and a 2 mol kg^{-1} NaCl solution. Several trajectories are run at different temperatures as indicated in the legend. The potential energy is monitored. It goes up (down) when ice melts (grows). In this example ice grows below 242 K and melts above 245 K. Therefore, the coexistence temperature is narrowed down to $(243,5 \pm 1,5) \text{ K}$.

Tabla 5.1. Obtained coexistence points of the studied equilibrium lines. For each of them, the direct coexistence method used is specified in parentheses. The numbers in parenthesis indicate the estimated statistical error. In the EDC method the error is given by the standard deviation of the concentration after convergence. For the NdDC case the temperature error is given by the temperature grid used to narrow down coexistence whereas the concentration error is less than one per cent due to the large portion of solution employed in the simulations (see Fig. 5.3).

Ice Ih - NaCl(aq) equilibrium line (NdDC)	
m (mol kg ⁻¹)	$T - T_m$ (K)
0.5	-1(1)
1.0	-3(1)
2.0	-6.5(1.5)
3.0	-13(3)
4.0	-18(3)
Ice Ih - NaCl(aq) equilibrium line (EDC)	
m (mol kg ⁻¹)	$T - T_m$ (K)
1.4(2)	-5
2.2(2)	-10
2.6(2)	-10
3.3(2)	-15
3.4(2)	-15
3.9(2)	-20
4.1(2)	-20
4.7(2)	-25
5.0(2)	-30
NaCl·2H ₂ O - NaCl(aq) equilibrium line (EDC)	
m (mol kg ⁻¹)	$T - T_m$ (K)
9.17(25)	70
8.86(25)	60
8.36(20)	50
8.25(25)	40
8.04(40)	30
7.90(40)	20
NaCl - NaCl(aq) equilibrium line (EDC)	
m (mol kg ⁻¹)	$T - T_m$ (K)
2.6(4)	100
3.0(4)	48

5.4.3 EDC

In EDC runs we monitor NaCl concentration –computed as discussed in Section 5.3.5– until a convergence value is reached. In Fig. 5.8, we show the concentration as a function of time for a couple of EDC runs of the ice-solution equilibrium at 235 K. Starting from two different initial concentrations (2 and 4 mol kg⁻¹) the same equilibrium concentration (3,5 mol kg⁻¹) is reached. As it can be seen in Fig.

5. Phase diagram of the NaCl-water system from computer simulations

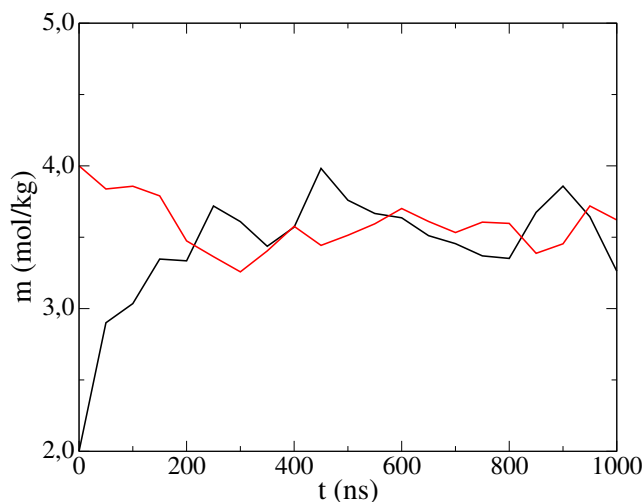


Figura 5.8. NaCl molal concentration versus time in EDC runs for the ice-solution equilibrium at 235 K. Starting from different initial concentrations the trajectories converge to the same equilibrium concentration.

8, once concentration is converged there are fluctuations of about $0,5 \text{ mol kg}^{-1}$ around the average value due to statistical noise. However, by averaging over the period in which the system is equilibrated we typically obtain the concentration with a smaller error, as reported in table 5.1 and shown in Fig. 5.1. Equilibration of the solution concentration requires long simulations, of the order of hundreds of nanoseconds. The same kind of convergence is achieved for all other points of the ice-solution line (not shown). Convergence starting from different concentrations gives us great confidence on the use of EDC to determine coexistence points. The obtained coexistence points are reported in Table 5.1.

We now compare the EDC and the NdDC results. In Fig. 5.1 we show with blue circles the points obtained with NdDC and with blue squares those computed with EDC for the ice-solution coexistence. We find an excellent agreement between both techniques for such coexistence line.

The main drawback of the EDC method is that it requires that the equilibrium concentration can be reached by partial melting/growth of the solid slab. One cannot, therefore, start the simulations from a concentration which is very far away from the final one. In NdDC, by contrast, one does not need to have an a priori feeling for the coexistence concentration: by looking at the tendency of the solid to grow or melt one can narrow down the coexistence conditions. Therefore, both methods are complementary: NdDC can be initially used to obtain a first coexistence point and then EDC can be employed to obtain other points along the coexistence line.

The EDC runs performed to obtain points of the $\text{NaCl} \cdot 2\text{H}_2\text{O}$ line are shown in Fig. 5.9, where one can see that runs converge to the same concentration, as desired, for $T > 270 \text{ K}$. The obtained coexistence points for such temperatures are reported in table 5.1. For lower temperatures we do not get the required conver-

gence. There are different factors that may slow down convergence. One is the diffusion of the liquid. As shown in Fig. 5.10, the diffusion coefficient of the solution components quickly drop when either concentration increases or temperature goes down. This makes the $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution experimental coexistence region, which lies at low temperatures and high concentrations, difficult to access by simulations. We have also tried to access that region with NdDC simulations but we found no conclusive answer.

However, one may wonder why we could compute coexistence points for the ice-solution line at low temperatures near the experimental eutectic point but not for the $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution one. One possibility is that, other than the diffusion of the solution, one has to take into account the dynamics of the solid-solution interface. It seems reasonable that the $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution interface advances/recedes much slower than the ice-solution one, due to the higher structural complexity of $\text{NaCl}\cdot 2\text{H}_2\text{O}$ (three components) as compared to ice (one component). Another possibility is that the $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution line bends down almost vertically at low concentrations as suggested by the first three noisy pink points in Fig. 5.1. In such case the simulation line would not follow the experimental one.

5. Phase diagram of the NaCl-water system from computer simulations

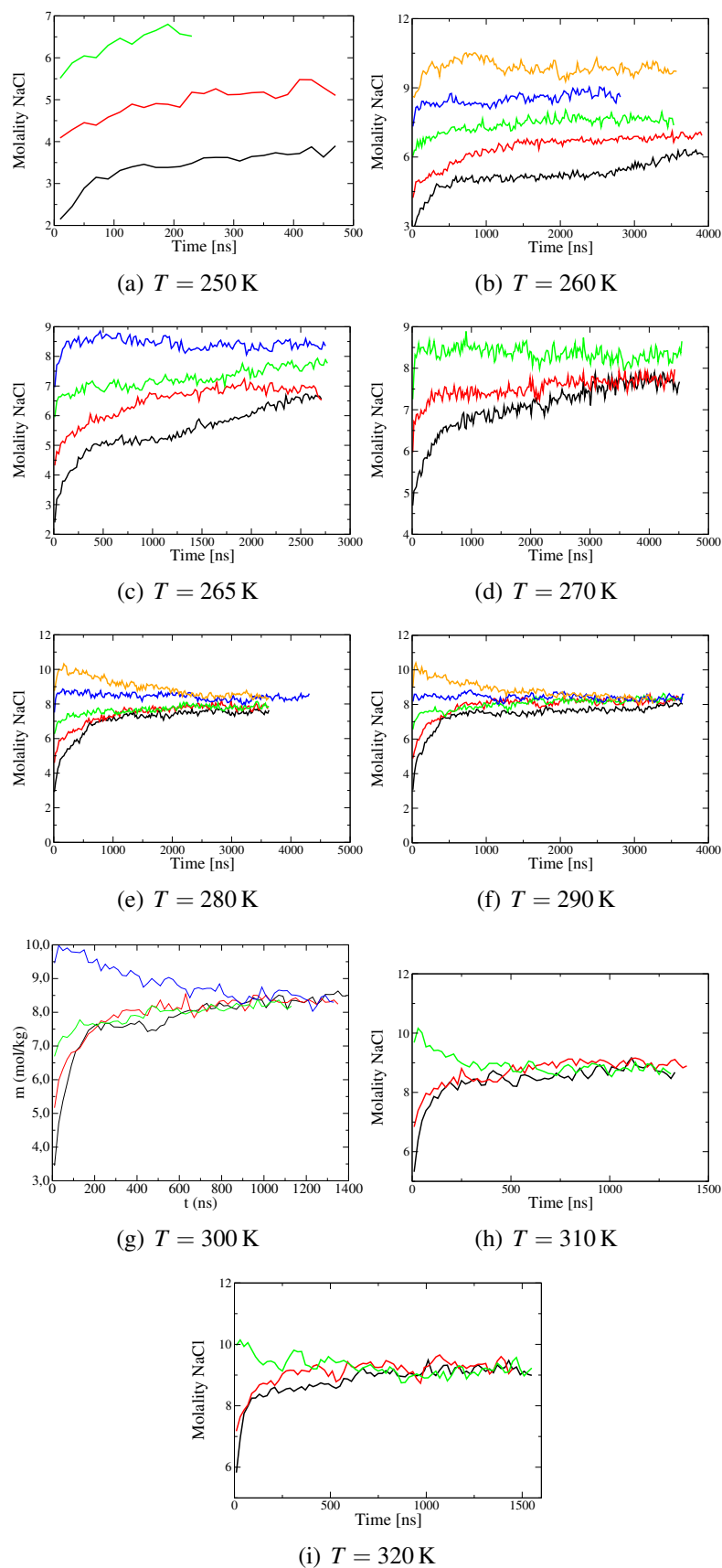
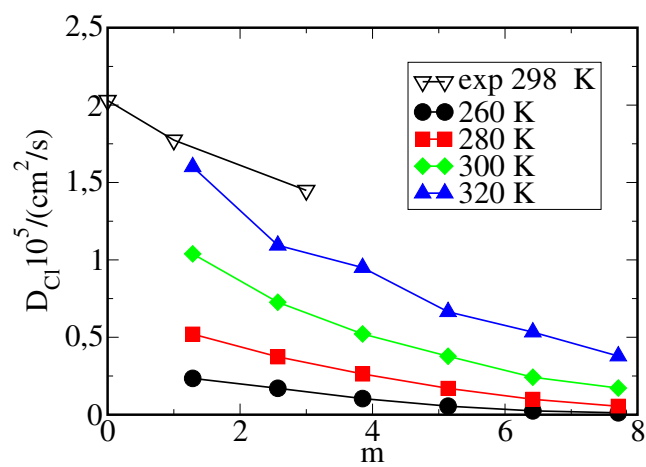
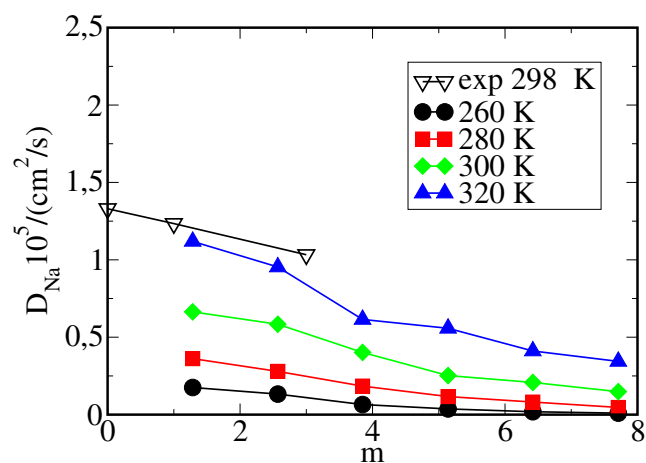
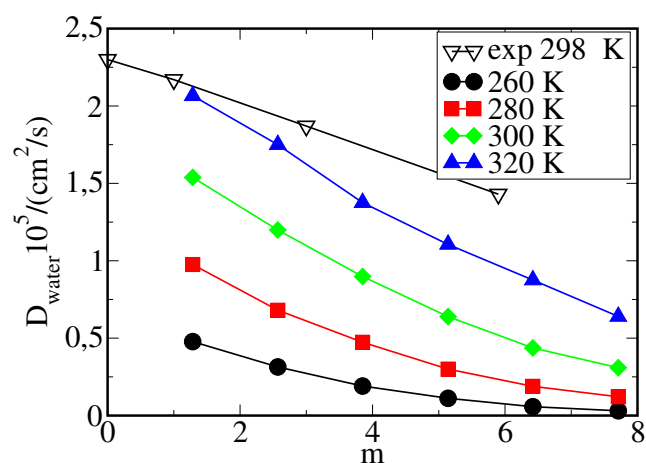


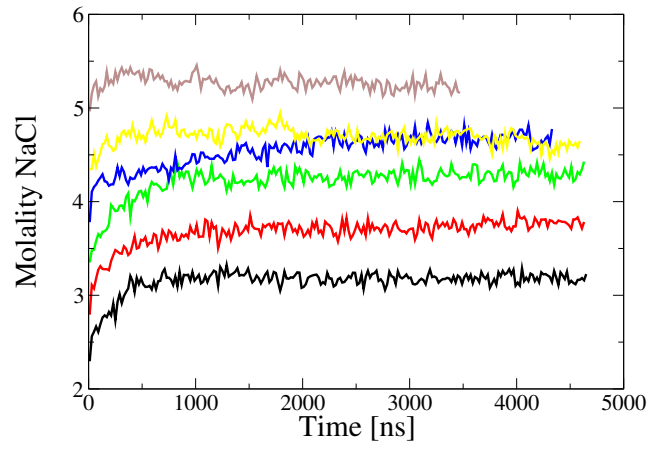
Figure 5.9. NaCl molal concentration versus time in EDC runs for the NaCl·2H₂O-solution equilibrium at several temperatures as indicated in the figure. Good convergence is reached for $T > 270$ K.

(a) Cl⁻(b) Na⁺

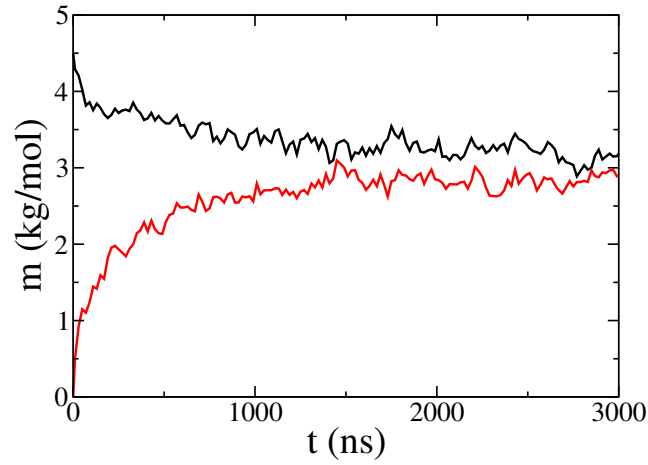
(c) Water

Figure 5.10. Diffusion coefficients of water and the Na⁺ and Cl⁻ ions as a function of temperature and salt molality. Simulation data are compared with experimental data for ions [66, 67] and water [68] self-diffusion coefficients.

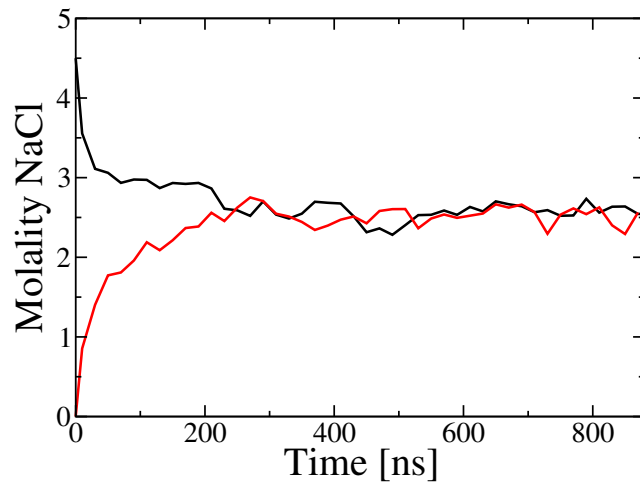
5. Phase diagram of the NaCl-water system from computer simulations



(a) 298 K; (100)



(b) 298 K, (110), red; (111), black



(c) 350 K; (110), red; (111), black

Figure 5.11. Evolution of composition in the EDC simulations of the NaCl-solution line for different temperatures and different exposed crystal orientations.

Computing the NaCl-solution line with DC simulations was quite problematic. There have been previous attempts to obtain NaCl-solution coexistence with EDC simulations [43, 32, 36, 37]. Even if the same model was used in these works, the solubility values reported in Refs. [43, 36, 32] were different between themselves and different from the consensus value obtained with free energy calculations [38]. However, in Ref. [37] an agreement with the consensus value was reached provided that long crystal slabs were used in the EDC simulations. Here, we follow the system size recommendations given in Ref. [37]. And we use TIP4P/2005 water whereas SPC/E [69] was employed in Ref. [37]. As shown in Fig. 5.11(a) our trajectories did not converge to the same concentration when we exposed the (100) crystal plane to the solution. This lack of convergence persisted for temperatures up to 400 K even for trajectories of a few microseconds (not shown). Therefore, we were unable to obtain an accurate NaCl-solution coexistence line with the EDC method when the (100) plane was exposed. The slow dynamics of growth/melting of the (100) plane of the rock salt has already been noted in previous works [70, 58]. However, when we exposed the (111) or the (110) planes the trajectories nicely converged to the same concentration at 298 and 350 K (see Figs. 5.11(b) and (c)). We also tried 250 K (not shown) but due to slow kinetics convergence was not reached at that temperature in the simulation time (a few microseconds).

The ionic arrangement in the (100) plane could explain the lack of convergence of simulations where such orientation is exposed. In Fig. 5.12 we show a snapshot of the ions at the (100) interface for a simulation at 298 K. The ions of the last complete ionic layer are shown in blue and cyan. The interface looks rather flat. Within a given plane, any ion is surrounded by 4 oppositely charged ones. On top of the last complete plane we observe isolated rectangular ionic islands (shown in red and orange). These islands remain static throughout the simulation (about 1 μ s), most likely due to the strength of the ion-ion interactions and to the geometry with which they are arranged at the interface, making it very costly to remove/add ions from/to the crystal.

By contrast to the (100) orientation, in the (110) and (111) planes some of the nearest neighbors of a central ion are equally charged. In the (111) plane, in fact, all 6 neighbours of a given ion are equally charged, whereas in the (110) plane two out of four of them are equally charged. This ionic arrangement makes the exchange of ions with the solution less energetically expensive as compared to the (100) case. In Fig. 5.12 we show that both (111) and (110) faces are rougher than the (100) face. Moreover, no rectangular islands are observed for the (110) and (111) faces in contact with the solution.

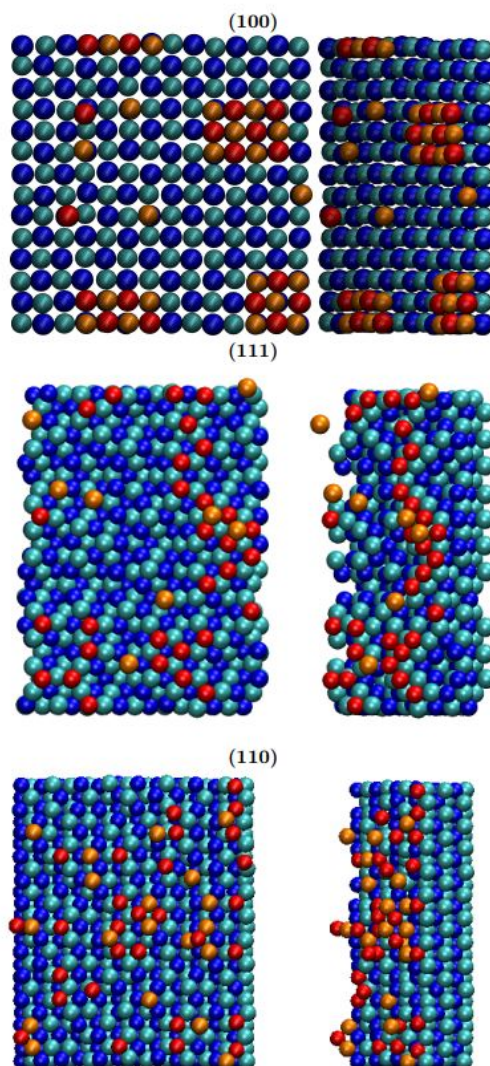


Figure 5.12. Front (left) and diagonal (right) view of the NaCl-solution interface at $T = 298$ K and ambient pressure. The ions of the last layers completely filled are shown with blue and cyan spheres. The atoms adsorbed on such layer are shown with red and orange spheres. Water molecules have been removed for the sake of visualization. The (100) orientation looks rather flat, and shows three rectangular islands, composed by 9, 12 and 12 atoms. These islands are kinetically quasi-arrested, meaning that their position and size remains the same on timescales spanning up to a μ s. Such islands are not observed for the other studied NaCl orientations, (111) and (110), which look rather rough as compared to the (100) face.

5.4.4 Phase diagram

In Fig. 5.1 we show with symbols the results obtained for all the DC runs performed in this work. Blue, orange, and pink symbols correspond to the coexistence of the solution with ice, NaCl and NaCl·2H₂O respectively. Lines, with the same

color code, correspond to the experimental coexistence line.

The agreement between simulation and experiment for the ice-solution line is remarkable. It slightly deteriorates near the eutectic point, but the agreement is excellent for most of the coexistence line. The $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution coexistence line seems to be a linear extrapolation of the experimental one, at least if one considers high-temperature points. However, the simulation line seems to bend down at low temperatures, when approaching the experimental line, although we could not confirm this due to slow convergence.

We include in Fig. 5.1 an empty orange triangle for the NaCl -solution coexistence taken from Ref. [38]. This point was obtained from free energy calculations and is in fair agreement with our EDC simulations (solid orange triangles). Free energy calculations, although costly and cumbersome, entail bulk phase calculations and are not affected by the slow dynamics of dissolution/recrystallization at the solid-solution interface. By contrast with the other two solids, the results are a bit disappointing for NaCl because the model predicts coexistence for concentrations significantly lower than the experimental ones. This means that the NaCl solid stability is overestimated as compared to that of the solution. Also the melting point of the NaCl crystal is overestimated (by about 200 K) by the model [59]. This suggests that ion-ion interactions are perhaps too strong. The ice-solution coexistence is not affected by this problem because the interaction between ions in solution is screened by water molecules. It may seem in principle surprising that ion-ion interactions do not have a strong effect on the ice-solution coexistence line. However, this statement is supported by three observations: (i) that the ice-solution line is well captured by a model that does not correctly predict the NaCl -solution coexistence; (ii) that ion pairing is very rare up to deeply supersaturated solutions [71]; (iii) most definitely, that a forthcoming publication using the same water model but ions with rescaled charges predicts a very similar ice-solution coexistence line (only in the vicinity of the eutectic point mild differences are found) [72]. The latter evidence strongly supports the idea that even if ion-ion interactions are not properly tuned, the ice-solution line can be well described given that ions do not closely see each other in solution, at least up to the eutectic concentration.

5.5 Summary and Conclusions

In this work we use the Direct Coexistence method to obtain, by means of molecular dynamics simulations, the coexistence between aqueous NaCl solutions and three solid phases: ice, NaCl and $\text{NaCl}\cdot 2\text{H}_2\text{O}$. For the ice-solution line we use two different Direct Coexistence approaches: one where we narrow down the coexistence temperature for a given concentration and another one in which we equilibrate the concentration for a given temperature. We find that both approaches are equivalent and use the latter to obtain coexistence points for the other two lines. The agreement between the model prediction and the experiment is ex-

5. Phase diagram of the NaCl-water system from computer simulations

cellent for the ice-solution line. The model $\text{NaCl}\cdot 2\text{H}_2\text{O}$ -solution line seems to be a linear extrapolation of the experimental one at high temperatures. However, at low temperatures, when approaching the experimental curve, the simulation line seems to bend down, although we could not confirm this point due to slow kinetics. In the NaCl-solution case, we were not able to get converged results with direct coexistence simulations due to the slow kinetics of dissolution-recrystallization at the solid-solution interface when the (100) plane was exposed. By contrast, convergence was reached for the (111) and (110) planes. The more energetically favourable ionic arrangement in the (100) plane could explain the slow convergence kinetics for this plane. Direct coexistence simulations for the other two planes are in good agreement with independent free energy calculations. The coexistence concentration is underestimated by the model, which is a sign that the stability of the solid is overestimated. This result suggests that the ion-ion interactions could be too strong in the model.

There are different possibilities to improve a solution model where ion-ion interactions seem to be over represented, like scaling down ion charges [73, 60], including polarizability [74, 42] or tuning cross dispersive interactions [39, 40].

In any case, all in all, the TIP4P/2005-JC model does a reasonable job in describing the phase diagram. Further work is required to develop an $\text{NaCl}/\text{H}_2\text{O}$ model that correctly predicts all coexistence lines and other thermodynamic and dynamic properties [41, 74, 75, 42, 76, 77]. A significant effort is being devoted to the development of accurate aqueous solutions electrolytes [74, 42]. Be it as it may, having a first global overview of the equilibrium phase diagram for a given model of water-NaCl mixtures is a good starting point for future model improvements and for studies of dynamics, crystal nucleation and crystal growth in such an important system.

5.6 Acknowledgments

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Chapter 6

Freezing point depression of salt aqueous solutions using the Madrid-2019 model

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6.1 Abstract

Salt aqueous solutions are relevant in many fields, ranging from biological systems to seawater. Thus, the availability of a force field that is able to reproduce the thermodynamic and dynamic behaviour of salt aqueous solutions would be of great interest. Unfortunately, this has been proven challenging, and most of the existing force fields fail to reproduce much of their behaviour. In particular, the diffusion of water or the salt solubility are often not well reproduced by most of the existing force fields. Recently, the Madrid-2019 model was proposed, and it was shown that this force field, that uses the TIP4P/2005 model for water and non integer charges for the ions, provides a good description of a large number of properties, including the solution densities, viscosities and the diffusion of water. In this work, we assess the performance of this force field on the evaluation of the freezing point depression. Although the freezing point depression is a colligative property that at low salt concentrations depends solely on properties of pure water, a good model for the electrolytes is needed to accurately predict the freezing point depression at moderate and high salt concentrations. The coexistence line between ice and several salt aqueous solutions (NaCl, KCl, LiCl, MgCl₂ and Li₂SO₄) up to the eutectic point is estimated from direct coexistence Molecular Dynamics simulations. Our results show that this force field reproduces fairly

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well the experimentally measured freezing point depression with respect to pure water freezing for all the salts and at all the compositions considered.

6.2 Introduction

When a solute is added to water, the freezing point of water decreases. The difference between the freezing temperature of pure water and that of a solution is denoted as freezing point depression. The freezing point depression caused by an electrolyte is larger than that of a non-electrolyte at the same molality (i.e., mols of solute per kilogram of solvent). This is due to the fact that electrolytes when dissolved into water dissociate into ions, thus generating more particles in solution. If ideal behavior is considered, the freezing point depression is proportional to the number of ions generated when dissolved (i.e., 2 for a 1:1 electrolyte and 3 for a 1:2 electrolyte). The constant of proportionality is related to properties of pure water and its experimental value is 1.86 K per molal unit. Not surprisingly, electrolytes are in fact often used to avoid the formation of ice in roads, since when salt is added water only freezes at temperatures below 0 °C. In the particular case of NaCl, the largest freezing point depression is reached at the eutectic point which is found at about 21 K below the melting point of pure water. This is the minimum temperature at which a NaCl aqueous solution could be present as the stable phase. At room pressure the solubility of salts in ice is practically zero and for this reason when water freezes from an ionic solution one obtains almost pure ice (a quite small amount of ions can incorporate into the ice at the micro-molar range at best [1, 2]). At the freezing temperature the chemical potential of water in pure ice is equal to that of water in the ionic solution. Thus the freezing point depression gives some information about the activity of water in the ionic solution.

Liquids can be supercooled [3], and this is true for pure water and for ionic solutions. When liquids are broken in small droplets of the order of a few microns of radius they can be supercooled up to 40 K below the freezing temperature. The degree of supercooling depends on the size of the droplets and on the velocity of cooling. Sometimes the temperature at which these droplets freeze is denoted as the freezing temperature (although this is a kinetic definition, not a thermodynamic one, and for this reason the term homogeneous nucleation temperature is preferred). Nevertheless, the term melting temperature is reserved for the temperature at which the chemical potential of water is identical in the two phases (ice and solution) [4]. In this work we shall use the concept freezing temperature in a thermodynamic way (i.e., where the chemical potential becomes identical in both phases), which corresponds to that denoted as melting temperature in kinetic studies of freezing.

Determining the freezing point depression from computer simulations is challenging from a technical point of view. A possible route is to determine the chemical potential of ice (for a certain pressure) as a function of the temperature,

and that of water in the solution (for a certain pressure and composition) as a function of the temperature and to analyze the temperature at which both chemical potentials are identical. This route is certainly possible, but somewhat cumbersome. One needs to evaluate the chemical potential of water in the solid phase using for instance Einstein crystal methods [5, 6], and the chemical potential of water in solution. Determining the chemical potential of water in an ionic solution (and the chemical potential of the salt) is also possible as it has been shown over the last few years but it is certainly a challenging and rather difficult calculation [7, 8]. One wonders if another simpler route would be possible. An interesting possibility is the use of the direct coexistence method [9, 10]. This method has proved to be successful in determining the freezing temperature of pure water, and one could imagine that the method could be applied to electrolyte solutions. In fact, Jungwirth started fifteen years ago to study the freezing of water from an ionic solution [1, 11] (paying special attention to brine rejection from the ice) and this has been followed by other authors [12, 13, 14]. In 2008 Kim and Yethiraj [15] performed a pioneering study where the freezing point depression was determined from computer simulations using the direct coexistence method, putting together ice and a concentrated solution of the electrolyte and waiting to reach the equilibrium running for about 50 ns (a tour of force at that time). More recently Conde, Rovere and Gallo have also illustrated the feasibility of direct coexistence studies to obtain the freezing point depression [16] by using runs of up to 300 ns. In this case instead of waiting to reach equilibrium, it was determined if the ice grew or melted for a certain initial concentration of salt. A similar approach was used by Soria *et al.* [17] who also showed that the freezing temperature found from free energy calculations was identical (within statistical uncertainty) to that obtained from direct coexistence simulations for a certain concentration of salt. In the work of Soria *et al.* [17] kinetics aspects of the nucleation of ice in salty water were also studied, and nucleation rates were estimated using the seeding technique [18].

Although these pioneering works have illustrated the possibility of using direct coexistence as a systematic study of the relation between the concentration of the electrolyte and the freezing temperature, it has not yet been applied to different salts and types of electrolytes. Most of the force fields proposed so far for electrolytes were designed to reproduce the density of the solution and the hydration free energy using rigid non-polarizable models to describe water, as for instance TIP3P [19], TIP4P-Ew [20] or SPC/E [21]. For the ions a Lennard Jones center is typically used with an integer charge (in electron units, e). Probably the force field proposed by Joung and Cheatham is now the most popular [22]. Properties like the solubility, viscosity and diffusion coefficient of water were not used as target properties. How these force fields perform for these properties? The short answer is, not too well.

Concerning the solubility, it has become clear that most of the force fields predict a rather low solubility (sometimes being twice smaller than the experimental one and sometimes being ten times smaller). [23, 24, 25, 26, 27] It has also fallen into place that the ion-pairing and precipitation often observed

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in simulations of ionic solutions was due to a too low solubility of the force field [28, 29, 30, 31]. In fact the solubility of a salt in water, for a certain force field, is not necessarily equal to the experimental one [8]. In general the trend is that the solubility is too low, and the ion pairing too high. Concerning the viscosity, it is getting across that common force fields overestimate the increase in the viscosity due to the addition of salt, when compared to experiments [32, 33]. Finally concerning the diffusion coefficient of water, it was pointed out by Yethiraj and coworkers [34] that most of the force fields (including polarizable ones) produce a larger decrease on the diffusion coefficient of water than the experimental one. How to remedy this situation? In 2014 Kann and Skinner [35] suggested that using scaled charges for the ions (i.e. for a 1:1 electrolyte assigning charges smaller than one in electron units) improved the description of the diffusion coefficient of water in ionic solutions. The use of scaled charges was first advocated by Leontyev and Stuchebrukhov [36, 37, 38] and was denoted as electronic continuum correction (ECC). They suggested to use a scaled charge of $0.75 e$, that is obtained from a theoretical argument which requires the dielectric constant of water at very high frequencies (when only electrons can reply to a fast oscillating electric field). This idea was also advocated by Jungwirth and coworkers [39, 40, 41, 42, 43], and also implemented by several groups [44, 45, 46, 47]. Following this line of research in 2017 we proposed a force field for NaCl in water [48] (with water described by the TIP4P/2005 model [49]) that used the concept of scaled charges. Our motivation was that maybe the charges used to describe the dipole moment surface were not convenient to describe the potential energy surface [50, 51]. In 2019 we extended this idea to many different electrolytes (with stoichiometry 1:1 and 1:2), and the force field was denoted by Madrid-2019 [33, 52, 53]. The value of the scaled charge in this case was $0.85 e$, because this value allows to recover the correct Debye-Huckel law, as shown by Kann and Skinner [35], i.e., it compensates the deficiencies in the dielectric constant of TIP4P/2005. It was found that the use of scaled charges improved the description of the viscosities, diffusion coefficients of water, activity coefficients and solubilities. For example, the solubility of NaCl for the Madrid-2017 model [48] is estimated to be 5.7 mol kg^{-1} at room conditions, in reasonable agreement with the experimental solubility, 6.1 mol kg^{-1} [54]. We expect a similar value for the Madrid-2019 model, as the change in the parameters between both models is small. For the remaining salts, the solubility has not yet been calculated. We should note that Tanaka and coworkers [55] have recently shown that, when properly designed, force fields with integer charges can also reproduce the experimental value of the solubility. As a counterpart, the use of scaled charges deteriorates the prediction of hydration free energies [56], and is not recommended either for molten salts or for the solid phase. [8, 57]

The idea of scaled charges finds a molecular basis on the fact that the calculated charge of the ions from ab-initio studies is typically in the range of $0.8 e$ (for anions) and $0.9 e$ (for cations) [58, 59]. Thus it seems that the use of non integer charges (an approximation often used by the community which performs simulations of ionic liquids [60]) seems to improve the description of electrolyte

solutions. The scaled charge approach (or ECC) can be regarded as an approximation of zero order. As a more elaborated approach one could use models that explicitly use the concept of charge transfer between the ions and water, as it has been shown by Rick *et al.* [61, 62] and by Berkowitz *et al.* [59].

In this work we have two goals. The first one is methodological. We will explore the possibility of determining the freezing point depression by using direct coexistence method to determine if this technique can be used to obtain reliable results using the current computational resources, that allow runs of the order of the microsecond. We shall follow the methodology of Kim and Yethiraj [15], so that ice will be put in contact with an ionic solution and simulations will be performed until the system reaches the equilibrium. For a two component system this is a quite useful approach since according to the Gibbs phase rule, two phases can be at equilibrium for an imposed value of the pressure and temperature. That was also illustrated by Espinosa *et al.* [27] to determine the solubility of a salt and by Kolafa [63] for a system of a solid (NaCl) and an ionic solution (NaCl in water) where simulations were performed until the system reached the equilibrium.

It is interesting to point out that the melting temperature of ice Ih for the TIP3P model is around 150 K [64], and for SPC/E is 215 K [65]. Therefore, the simulations to study the freezing point depression should be performed at extremely low temperatures, where the diffusion of water will be terribly slow and the direct coexistence method would be in trouble. Thus it does not seem a good idea to use these water models (neither their force fields) for this purpose. A better choice would be the TIP4P-Ew model [20] with a melting point of about 244 K [66] and an even better choice would be the TIP4P/2005 with a melting temperature of 250 K [67]. This model is convenient as water is still able to diffuse reasonably well in the range 210 K-250 K (i.e. for supercoolings up to 40 K). Thus the use of TIP4P/2005 for computer simulations studies of freezing point depression is a good choice for two reasons: its melting temperature is not too low, and a force field for electrolytes (Madrid-2019) is available for this water model. TIP5P [68] and/or TIP4P/Ice [69] could also be considered as promising models for freezing point depression as their melting points are quite close to the experimental one. However, there are not force fields of salts explicitly developed for these water models and in the case of TIP5P, ice II seems to be more stable [64] than ice Ih at room pressure.

There is a second goal in this work. We want to test if scaled charges are able or not to predict reasonably well the freezing point depression of different salts. It seems interesting to analyze if the improvement gained by using scaled charges in properties like viscosity, solubility and diffusion coefficient of water has as a consequence a poor performance of other properties like the freezing point depression. As it will be shown in this work, this fear is not justified and the model performs quite well. The good agreement found with experiments also provides an indirect indication that the activities of water should not be too far away from the experimental ones. We hope that freezing point depression will be incorporated as another test property to be checked when proposing a new force

field for electrolytes in water.

6.3 Methods

6.3.1 Direct coexistence method

The freezing point depressions of the salt aqueous solutions are estimated in this work using the direct coexistence technique [70, 9]. Briefly, this method consists in building a simulation box in which two phases (in this case ice and the electrolyte aqueous solution) are initially placed next to each other, and following the evolution of the system at different thermodynamic conditions. Depending on the thermodynamic ensemble used in the simulations and the number of components in the system, the fate of the interface changes: it can either reach a stable state or irreversibly evolve towards one of the two phases.

At a given thermodynamic state, two (or more) phases (I , II) are in equilibrium when the chemical potential of all the components of the system (two in our case) are equal in the coexisting phases:

$$\begin{aligned}\mu_1^I(p, T, x_1^I) &= \mu_1^{II}(p, T, x_1^{II}) \\ \mu_2^I(p, T, x_2^I) &= \mu_2^{II}(p, T, x_2^{II})\end{aligned}\tag{6.1}$$

Here μ_i^α and x_i^α are, respectively, the chemical potential and mole fraction of component i in phase α .

The Gibbs phase rule imposes constraints on the number of phases that can coexist and applies both to single- and multiple-component systems. It states that for a system with C components and P phases, the number of independent variables or degrees of freedom F is given by:

$$F + P = C + 2\tag{6.2}$$

Consequently, in one-component systems ($C = 1$), if both p and T are imposed ($F = 2$), only one phase can be stable. This explains why in an one-component system an interface cannot be stabilized in NpT simulations. In the NVT ensemble, though, only the temperature is fixed ($F = 1$), and thus, in these conditions two phases of a one-component system can coexist [71]. On the contrary, in a two-component system ($C = 2$), as for example the salt aqueous solutions considered in this work, we can have two phases in equilibrium even when both p and T are fixed ($F = 2$). In this case, the compositions of the two phases in coexistence evolve until the chemical potentials of each component are equal in the two phases (Eq. 6.1). Even though we have written the condition of equal chemical potential of the component 2 in terms of its mole fraction (x_2^I and x_2^{II}), it could have been equally written in terms of the mole fractions of component 1 (x_1^I and x_1^{II}) because the mole fractions add up to one in each phase ($x_1^I + x_2^I = 1$ and $x_1^{II} + x_2^{II} = 1$). Thus, in two-component systems, there is only one independent variable that adjusts the

compositions of the two coexistence phases. Note that it would also be possible to perform the direct coexistence simulations in other ensembles such as NVE. In this case the pressure, temperature and composition will evolve to equilibrium. However using the NVE ensemble has the disadvantage that special care must be taken so that the dimensions of the unit cell in the directions parallel to the interface are chosen commensurate with the equilibrium unit cell at the equilibrium temperature and pressure [71].

The fact that in two-component systems two phases can be in equilibrium at fixed p and T can be exploited in the direct coexistence method to calculate the equilibrium compositions at coexistence [27]. One simply needs to build a simulation box in which the two phases are initially in contact with each other and let the system evolve. The ice slab will grow or melt depending on the initial conditions, releasing/absorbing water molecules to/from the salt solution, until the liquid phase reaches the equilibrium composition. The only subtlety is that in finite systems as those used in simulations the initial conditions must be close enough to coexistence, so that the system is able to reach equilibrium before exhaustion of any of the coexistence phases. As mentioned in the introduction, an alternative is to follow the evolution of the interface for an initial salt concentration to bracket the concentration at equilibrium [16]. In this work, we will follow the equilibrium route.

6.3.2 Model and simulation details

The interactions in the salt aqueous solutions were described using the recently proposed Madrid-2019 model [33]. This force field describes water and the sulfate ions as rigid and non-polarizable. Water is modelled with the TIP4P/2005 potential [49] and ions are represented by Lennard-Jones centers and scaled point charges ($0.85 e$ at the monovalent and $1.7 e$ at the divalent ions) that, in an effective way, account for the polarization effects in the solution.

m_i (mol kg ⁻¹)	N_{an} 1:1 and 2:1	N_{cat} 1:1 and 1:2	N_{an} 1:2	N_{cat} 2:1
1		60		-
2		120		240
3		180		360
4		240		-
6		360		-

Table 6.1. Number of ions in the systems depending on the salt compound stoichiometry and the initial molality, m_i . N_{an} is the number of anions and N_{cat} the number of cations. Compounds with stoichiometry 1:1 are NaCl, KCl, LiCl, with stoichiometry 1:2 we have MgCl₂ and with stoichiometry 2:1 Li₂SO₄.

6. Freezing point depression of salt aqueous solutions using the Madrid-2019 model

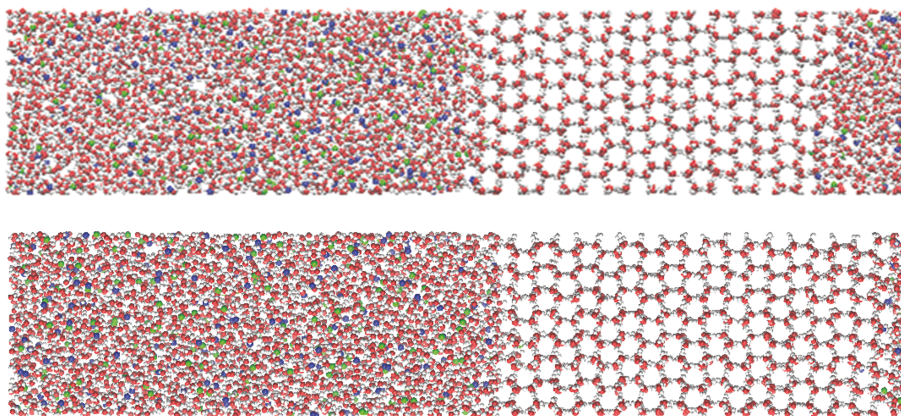


Figure 6.1. Initial (top) and final (bottom) configuration of an ice slab in contact with a LiCl solution at $T = 220$ K and room pressure. The initial salt concentration was set to $m = 4 \text{ mol kg}^{-1}$, which is below the equilibrium concentration at those thermodynamic conditions. In this case, the ice slab grows, incorporating some solvent from the solution until the salt concentration of the solution reaches the coexistence value at the chosen conditions of temperature and pressure, which is roughly $m = 4.48 \text{ mol kg}^{-1}$.

The initial configuration was built by placing a slab of 2048 molecules of ice I_h in contact with a salt aqueous solution containing 3330 water molecules and a varying number of ions depending on the temperature. The initial configuration of ice I_h with proton disorder and almost zero dipole moment satisfying the Bernal-Fowler [72] rules was generated using the algorithm proposed by Buch *et al.* [73]. Initial solution concentrations between 1 and 6 mol kg^{-1} were considered to cover temperatures within the range $T = 200 - 247$ K. The corresponding numbers of ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Cl^- and SO_4^{2-}) are given in Table 6.1. The block of ice was placed exposing the basal plane to the salt solution, and removing the overlaps between particles that lead to high repulsive forces. The freezing point does not depend on which crystallographic plane is exposed, it only changes the speed of growth/melting of the surface [74, 75]. The edges of the simulation box are approximately $L_x \approx 3.6 \text{ nm}$, $L_y \approx 3.1 \text{ nm}$ and $L_z \approx 15.5 \text{ nm}$. The ice-solution interface was aligned perpendicularly to the z axis. The dimensions of the ice slab are $3.6 \text{ nm} \times 3.1 \text{ nm} \times 5.9 \text{ nm}$. Note that the width of the ice slab is large enough to avoid finite size effects on the direct coexistence method [27].

The system is then allowed to evolve. The simulations are performed using the Molecular Dynamics GROMACS package [76] in the NpT ensemble, so that the ice slab is able to adjust its lattice constants by varying the edges of the simulation box in the two dimensions parallel to the interface. Previous works have shown that even though the pressure in the longitudinal and transversal directions to the interface are not equal due to the presence of the interface, direct coexistence simulations in the NpT ensemble give the correct results if the longitudinal dimension of the simulation cell is sufficiently large so that the contribution of the

interface to the pressure tensor is small [71, 77]. The pressure was set to $p = 1$ bar and was controlled using an anisotropic Parrinello-Rahman barostat [78], with a relaxation time of 2 ps and a compressibility of 10^{-6} bar. The temperature was set using the Nosé–Hoover thermostat [79] with a relaxation time of 2 ps. The equations of motion were integrated using the velocity-Verlet algorithm using a time step of 2 fs. To deal with the long range electrostatic interactions the particle mesh Ewald summations [80] were used. The cut-off distance for the dispersive and the real part of the electrostatic interactions was set to $10 \text{ \AA}$. Standard long range corrections (LRC) were added to the calculation of Lennard-Jones (LJ) interactions. LRC were calculated using the mean density of the system. Although this is not strictly correct for inhomogeneous systems, the densities of the solution and of ice are rather similar. The geometry of the water molecules was constrained with LINCS, using a sixth order expansion and a maximum of 4 iterations [81, 82], except for the sulfate solution for which SHAKE [83] was used.

The initial interface will evolve to reach the equilibrium concentration at the simulated temperature and pressure. If the concentration of the solution is higher than that at coexistence, the ice slab will melt, releasing water to the solution to reduce its salt concentration. On the contrary, if the initial concentration is lower than that at equilibrium, the ice slab will grow to increase the concentration of the solution. The initial and final configurations of a sample interface in which an ice slab is in contact with a LiCl solution at $T = 220 \text{ K}$ are shown in Figure 6.1.

We consider that the system has reached equilibrium when the potential energy of the system, and the solution salt concentration remain, on average, constant. The concentration of the solution at equilibrium was estimated from the density profiles of water ($\rho_{wat}(z)$) and salt ($\rho_{salt}(z)$) measured along the z -coordinate that, in the chosen coordinate system, runs in the direction perpendicular to the ice-solution interface. The density profiles were evaluated by dividing the simulation box in 100 slabs of width $\Delta z = L_z/100$ and measuring the water or salt density in each of them:

$$\rho_i(z) = \frac{w_i(z + \Delta z)}{\langle L_x \rangle \langle L_y \rangle \Delta z} \quad (6.3)$$

where $w_i(z + \Delta z)$ is the mass of the water molecules (w_{wat}) or of the ions (w_{ions}) whose positions along the z -coordinate are between $z - \Delta z/2$ and $z + \Delta z/2$, and $\langle L_x \rangle$ and $\langle L_y \rangle$ are the average edge lengths of the simulation box in the directions parallel to the interface.

6. Freezing point depression of salt aqueous solutions using the Madrid-2019 model

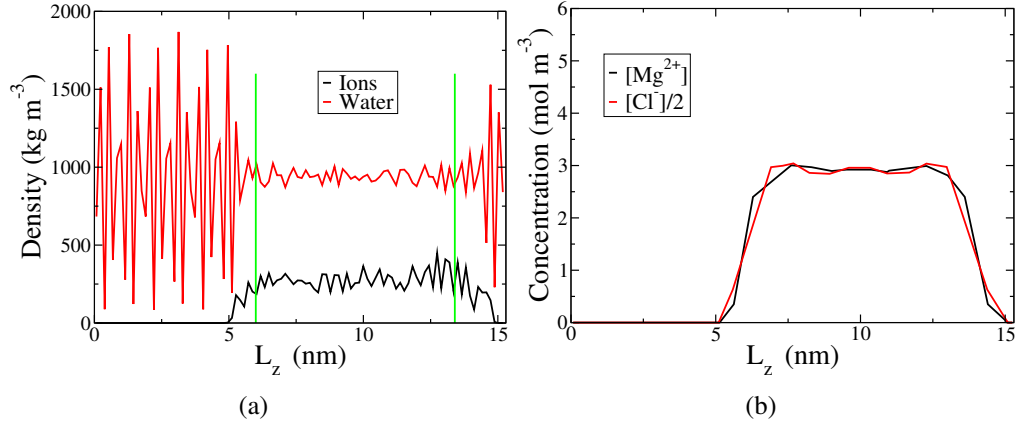


Figure 6.2. Density profiles of water and salt in the MgCl_2 system at $T = 215 \text{ K}$ and an initial concentration of salt 3 mol kg^{-1} . (a) The region comprised between the two vertical green lines was considered in the calculation of the molality. Results are averaged at times between 300 ns and 350 ns and the system is divided lengthwise in 100 bins. (b) Concentration profiles of each ion are shown separately to show that the system fulfills the requirement of local electrostatic neutrality. Results are averaged at times between 1000 ns and 1050 ns and 30 bins are considered. For aiding visualization, the concentration of Cl^- is divided by 2.

These density profiles were averaged over periods of 50 ns (500 frames). As an example, the equilibrium density profile of the MgCl_2 system at $T = 215 \text{ K}$ is shown in Figure 6.2 (a). From these plots it is easy to determine the region in which the solution exhibits bulk behaviour. Note that densities deviate significantly from the bulk at distances close to the interface, and these regions should not be taken into account in the estimates of the salt concentration in the liquid phase. From these densities one then can easily compute the salt concentration, e.g. the molality $m(z)$, using:

$$m(z) = \frac{\rho_{\text{salt}}(z)}{\rho_{\text{wat}}(z) \times M_{\text{salt}}}, \quad (6.4)$$

where M_{salt} is the molar mass of the ionic compound. As density profiles are measured in kg m^{-3} , the molar mass M_{salt} must be expressed in kg mol^{-1} units. The molality of the solution, m , is then estimated by averaging $m(z)$ over the slabs in which the solution behaves as bulk. As mentioned before, at equilibrium the molality remains stationary with time, fluctuating about the average equilibrium value. An example of the evolution of molality with time is shown in Figure 6.3. As can be seen, the salt concentration undergoes large fluctuations at short times, but oscillations become smaller and the molality adopts an average constant value at long times. The red vertical line marks the point from which the molality was averaged in the MgCl_2 system at $T = 215 \text{ K}$. This vertical line represents the time required to reach equilibrium (i.e where fluctuations in the concentration of the

solution are not larger than around 0.1 mol kg^{-1} of the equilibrium value). The uncertainty in the equilibrium salt concentration was estimated from the dispersion of the molality measured in these blocks. The error in the freezing point depression was estimated by assuming an uncertainty of 0.5 K in the freezing point of pure water, and adding to this an estimation of the uncertainty of the freezing point of the salt from the uncertainty in the molality. The total error in the given freezing point depression is about $0.75 - 1 \text{ K}$.

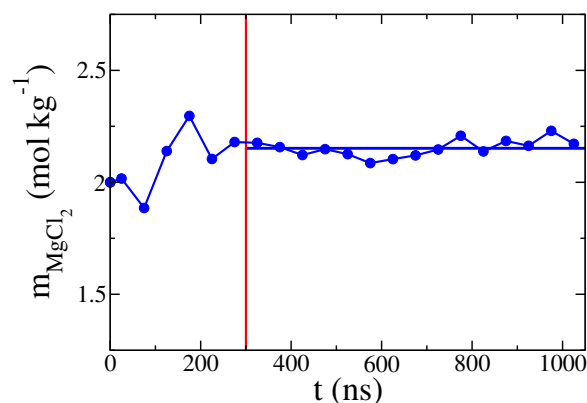


Figure 6.3. Molality as a function of time, t , in the solution of MgCl_2 with an initial concentration of 2 mol kg^{-1} in contact with an ice slab at $T = 232.5 \text{ K}$. The red line indicates where the equilibrium is reached (i.e., when fluctuations in the concentration of the solution are not larger than around 0.1 mol kg^{-1} of the equilibrium value, which is represented with a blue line).

The number density profiles of the ions are also useful to check that the system fulfills the requirement of local electrostatic neutrality, i.e., that the average net charge is zero in any slab sufficiently away from the interface. Number density profiles are shown in Figure 6.2(b). Although in the proximity of the interface with ice electroneutrality is not strictly satisfied (due to the different adsorptions of cations and anions) it can be seen that electroneutrality is satisfied in the bulk solution far away of the interface.

The time needed to reach equilibrium is stochastic and independent simulations at the same thermodynamic conditions and initial salt concentration can reach equilibrium at different times [27]. However, on average, simulations starting from conditions close to coexistence will generally equilibrate faster than those starting from conditions far away from the freezing point. If the chosen initial concentrations are too far from equilibrium, the whole ice slab can melt before reaching the equilibrium composition of the salt aqueous solution, or it can grow leaving a very small region of liquid, in which the bulk region is too narrow to properly evaluate the equilibrium salt concentration. Initial and final configurations of simulations exemplifying these two scenarios are shown in Figure 6.4. In either of these two situations, a new simulation box must be built but tweaking the initial composition of the fluid: if all the ice slab has melted, the salt concentration

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of the solution must be reduced and, on the contrary, if the solution region is too narrow, the initial salt concentration of the solution has to be increased.

When comparing with experiments, the melting temperature will be expressed as $\Delta T = T_m^{solution} - T_m$, where T_m is the melting point of pure water. In this way we account for the decrease in the melting point of water by the addition of salt. Note that the TIP4P/2005 exhibits a melting point of 250 K [67], i.e. about 23 K lower than the experimental value, 273.15 K. We will see that even though the absolute temperature at which freezing occurs for a given salt concentration is underestimated in absolute value, an excellent agreement is recovered when the temperature is measured with respect to the melting temperature of pure water.

6.3.3 Freezing point depression for an ideal mixture and estimation of the water activity

Once the melting point for a given salt at a given concentration is known, as a byproduct of the direct coexistence simulations, we can also obtain the water activity or, equivalently, the water activity coefficient at coexistence. The activity coefficient measures the deviation of the chemical potential of water in the solution with respect to an ideal solution.

As stated in Eq. 6.1, at coexistence the chemical potentials of the two components are equal in the two phases. The chemical potential of water in the solution can be expressed in terms of the water activity (a_{wat}):

$$\begin{aligned}\mu_{wat}^{solution}(T) &= \mu_{wat}^0(T) + RT \ln a_{wat} \\ &= \mu_{wat}^0(T) + RT \ln (\gamma_{wat} x_{wat})\end{aligned}\quad (6.5)$$

where $\mu_{wat}^0(T)$ is the chemical potential of pure water at the same conditions of p and T as the mixture. The chemical potentials are a function of the temperature and the pressure, but we leave out the pressure because all the simulations were done at 1 bar. In the last equality of Eq. 6.5, the activity is expressed in terms of the water molar fraction x_{wat} and the activity coefficient γ_{wat} . At coexistence, the chemical potential of water in the solid phase is equal to the chemical potential of water in the solution (Eq. 6.1). Assuming that the chemical potential of water in the solid phase is identical to that of pure ice (given the very small solubility of salts in ice) and taking into account the condition of chemical equilibrium (i.e., the same chemical potential for water in ice and in the solution at coexistence), one obtains:

$$\begin{aligned}\mu_{ice}^0(T) &= \mu_{wat}^0(T) + RT \ln a_{wat} \\ &= \mu_{wat}^0(T) + RT \ln (\gamma_{wat} x_{wat})\end{aligned}\quad (6.6)$$

If the mixture behaves as an ideal mixture the activity coefficient is equal to one, and the previous expression reduces to:

$$\Delta\mu^0(T) = \mu_{ice}^0(T) - \mu_{wat}^0(T) = RT \ln x_{wat}, \quad (6.7)$$

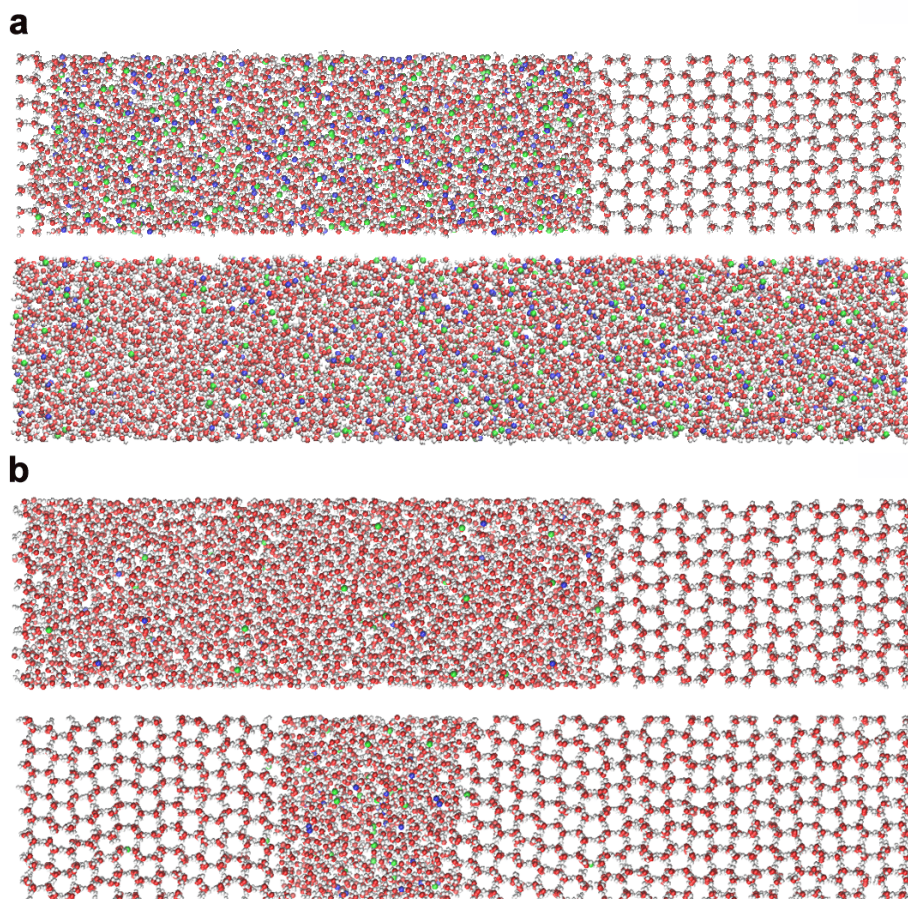


Figure 6.4. (a) Initial (top) and final (bottom) configurations of an ice slab in contact with a NaCl solution at $T = 243\text{ K}$ and room pressure. The initial salt concentration was set to $m = 6\text{ mol kg}^{-1}$, which is much higher than the equilibrium concentration at those thermodynamic conditions ($m = 2.13\text{ mol kg}^{-1}$). In this case, the ice slab melts completely. (b) Initial (top) and final (bottom) configurations of the same system as before but now setting the initial salt concentration to $m = 0.5\text{ mol kg}^{-1}$, which is much below the equilibrium concentration at those thermodynamic conditions. Now most of the system crystallizes, leaving a fairly narrow region for the solution phase.

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where the water molar fraction must be calculated taking into account the number of ions (instead of the number of salt molecules) [84]:

$$x_{wat} = \frac{n_{wat}}{n_{wat} + n_{ions,+} + n_{ions,-}}. \quad (6.8)$$

where n_{wat} is the number of moles of water and $n_{ions,+}$ and $n_{ions,-}$ are, respectively, the number of moles of positively and negatively charged ions. In Eq. 6.7, $\Delta\mu^0(T) = \mu_{ice}^0(T) - \mu_{wat}^0(T)$ can be obtained by thermodynamic integration from the freezing point of pure water using the expression:

$$\frac{\Delta\mu^0(T)}{RT} = - \int_{T_m}^T \frac{H_{ice}^0(T') - H_{wat}^0(T')}{RT'^2} dT' \quad (6.9)$$

Here H_{ice}^0 and H_{wat}^0 are the enthalpy (per mol) of ice and liquid water in the pure system, respectively. To obtain this expression we have used that at the melting temperature of pure system, T_m , the chemical potential of ice and liquid water are equal. As a first approximation, the freezing point depression of an ideal electrolyte can be computed assuming that the integrand of Eq. 6.9 is independent of the temperature and adopts the value at the melting point, so that the integral is trivial:

$$\frac{\Delta\mu^0(T)}{RT} = \frac{\Delta H_m}{RT_m^2} (T - T_m) \quad (6.10)$$

where $\Delta H_m = H_{wat}^0 - H_{ice}^0$ is the melting enthalpy. This equation can be solved in conjunction with Eq. 6.7 for different values of the water molar fraction x_{wat} , obtaining the freezing temperature at that composition if the solution were ideal:

$$\Delta T = \frac{RT_m^2}{\Delta H_m} \ln(1 - x_{ions}) \approx - \left(\frac{RT_m^2 M_w}{\Delta H_m} \right) \nu m \quad (6.11)$$

In the last step the logarithm was replaced by a Taylor expansion, valid for low concentrations ($\ln(1 - x_{ions}) \approx -x_{ions}$ and $x_{ions} \approx n_{ions}/n_{wat}$ when $x_{ions} \rightarrow 0$). ν is the number of ions in which the salt dissociates. We have also used that $m = \frac{n_{salt}}{n_{wat} M_w}$, $n_{ions} = n_{salt} \nu$, and $M_{wat} = 0.018015 \text{ kg mol}^{-1}$ is the molar mass of water. Note that Eq. 6.11 is the expression mentioned in the Introduction and that is often used to estimate the freezing point depression. As we will see later, Eq. 6.11 provides good estimates of the experimental freezing point depression up to 1 mol kg^{-1} for 1:1 electrolytes and up to 0.35 mol kg^{-1} for 1:2 or 2:1 electrolytes.

Alternatively, the integrand of Eq. 6.9 can be more rigorously evaluated if the dependence of the integrand of Eq. 6.9 is known. For that aim, we performed NpT simulations of ice and water at different temperatures along the $p = 1 \text{ bar}$ line. These data were then fitted to a second-degree polynomial. By plugging the fit in Eq. 6.9, we obtain that:

$$\begin{aligned} \frac{\Delta\mu^0(\Delta T)}{RT} = & 9.06 \times 10^{-3} \Delta T + 1.33 \times 10^{-6} \Delta T^2 + \\ & -4.28 \times 10^{-7} \Delta T^3 \end{aligned} \quad (6.12)$$

Note that the linear term of this expansion is given by $\Delta H_m/RT_m^2$. Thus, another estimate of the ideal freezing point depression can be obtained by solving Eq. 6.12 together with Eq. 6.7 for different values of the water molar fraction x_{wat} .

Finally, the activity of water can be obtained by substituting Eq. 6.12 in Eq. 6.6:

$$\ln a_{wat} = \left(\frac{\Delta\mu^0(\Delta T)}{RT} \right) \quad (6.13)$$

The activity of water in an electrolyte solution when in equilibrium with ice depends on the thermodynamic conditions (i.e. p and T), but not on the type of electrolyte in the solution [85, 4]. The logarithm of the water activity can be expanded as a polynomial function of the freezing point depression [86], whose first coefficient is $\Delta H_m/RT_m^2$.

As at constant temperature and pressure the chemical potentials of water and salt are related by the Gibbs-Duhem equation:

$$\begin{aligned} n_{wat}d\mu_{wat} + n_{salt}d\mu_{salt} &= 0, \\ d\ln a_{salt} &= -\frac{1}{mM_w}d\ln a_{wat} \end{aligned} \quad (6.14)$$

once the activity of water is known, the activity of the salt can also be obtained [86] by integration from very low salt concentrations. Note, however, that for performing this integration one needs to have accurate measurements of the freezing point depression at very low salt concentrations, something that is not possible using our direct coexistence simulations.

6.4 Results

The ice-solution equilibrium curves for NaCl, KCl, LiCl, MgCl₂ and Li₂SO₄ as a function of the salt concentration obtained in this work are given in Figure 6.5 and in Table 6.2. Before discussing these, we will show that our results are not significantly affected either by the use of the usual LRC for the LJ potential or by finite size effects. Firstly, to assess the effect of LRC, we repeated the calculations for the NaCl solution starting from a 4 mol kg⁻¹ concentration at $T = 236$ K using a longer cut-off of 12 Å with LRC. The evolution of the molality of the solution with time is shown in Figure 6.6. It can be seen that the equilibrium molality obtained with the 10 Å cut-off (4.07(0.08) mol kg⁻¹) is in agreement with that obtained with the 12 Å cut-off (4.03(0.08) mol kg⁻¹) within the statistical uncertainty of the simulations, see Figure 6.5 and Table 6.2. Consistently with this, in previous work, we found that the coexistence between ice and a NaCl solution obtained with a 9 Å cut-off and LRC is the same (within the statistical uncertainty), as that obtained with a cutoff of 13 Å and switching off the LJ LRC [90].

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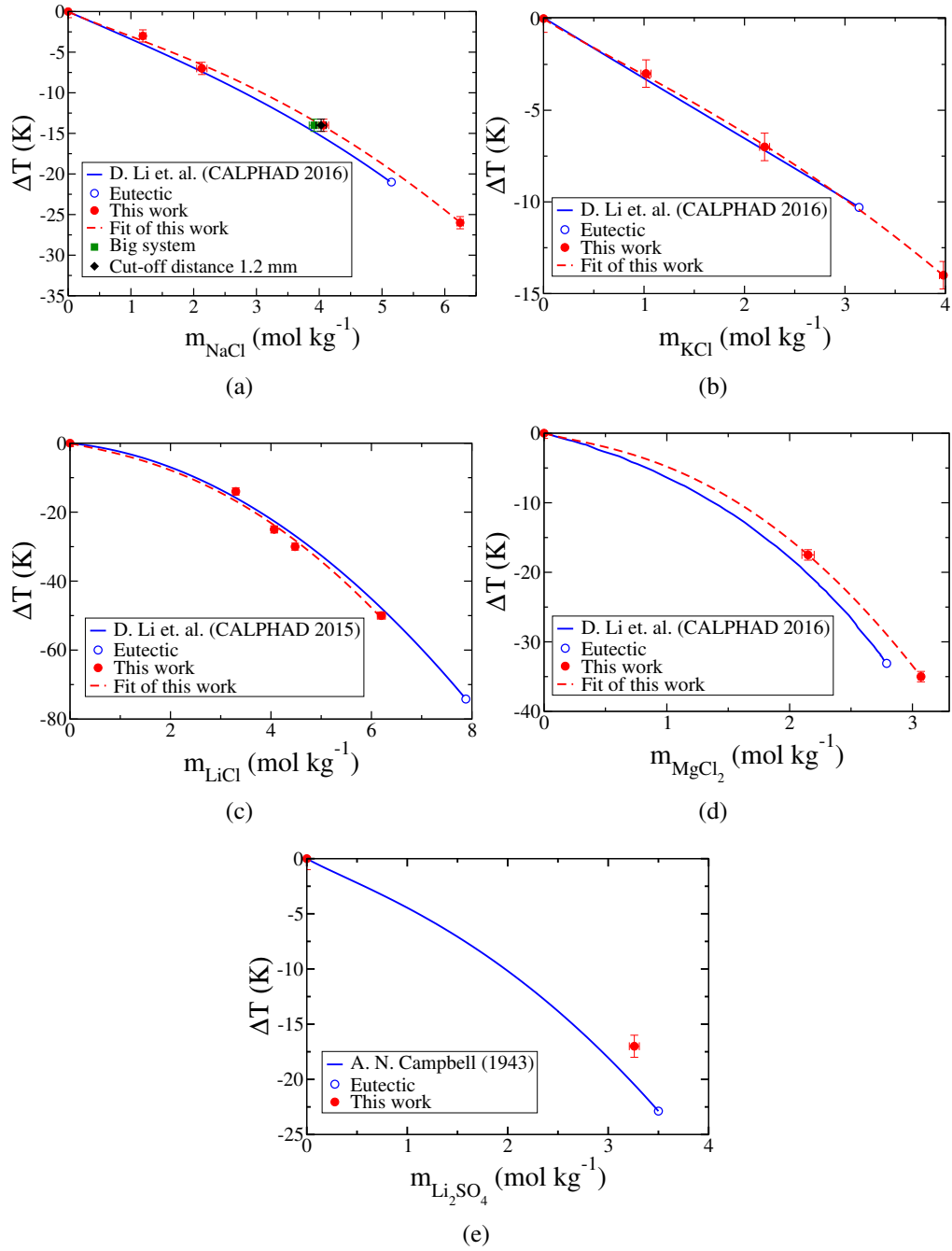


Figure 6.5. Freezing point depression of ice in contact with (a) NaCl, (b) KCl, (c) LiCl, (d) MgCl₂ and (e) Li₂SO₄ aqueous solutions as a function of salt concentration, as obtained from simulations using the Madrid-2019 model. Experimental data from the literature [87, 88, 89] (see references therein for the original sources of the experimental measurements) has been fitted to $\Delta T(m) = -v1.856m - bm^{1.5} - cm^2$, and this fit is shown for comparison (blue line).

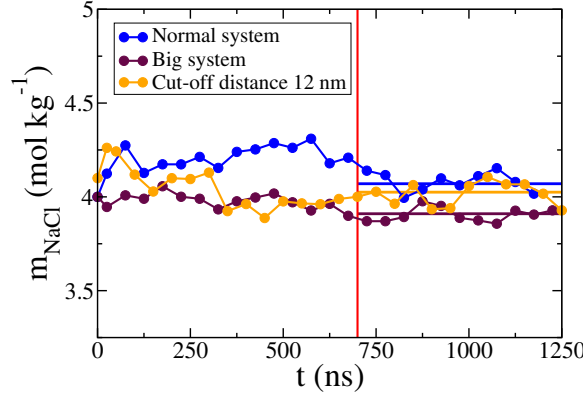


Figure 6.6. Evolution of the molality with time in the NaCl system at $T = 236\text{ K}$ in the three set ups of the simulation, namely using the system size adopted in this work ($3.6\text{ nm} \times 3.1\text{ nm} \times 11.7\text{ nm}$) using a $10\text{ \AA}$ and a $12\text{ \AA}$ cut-off, in both cases using the usual LRC to the LJ contribution, and in a system twice larger in the dimension parallel to the interface ($3.6\text{ nm} \times 3.1\text{ nm} \times 11.7\text{ nm}$) using a $10\text{ \AA}$ cut-off with the usual LRC to the LJ contribution. The equilibrium values are represented with a solid line.

Secondly, to make sure that our results are not significantly affected by finite size effects, we repeated the simulation by doubling the size of the ice slab and the solution along the z -axis for the NaCl system at $T = 236\text{ K}$. In this system an ice slab with 4096 molecules and $3.6\text{ nm} \times 3.1\text{ nm} \times 11.7\text{ nm}$ dimensions was put in contact with a solution containing 6660 water molecules, so that the system dimensions are roughly $3.6\text{ nm} \times 3.1\text{ nm} \times 30.5\text{ nm}$. The results obtained for both system sizes are the same within the statistical uncertainty of the simulations. In particular, the equilibrium concentration was found to be $4.07(0.08)\text{ mol kg}^{-1}$ in the small system and $3.92(0.08)\text{ mol kg}^{-1}$ in the large system.

Let us now look at how the simulated data compares with the available experimental measurements in the literature. To aid that comparison, the simulation freezing points were fitted to a polynomial function of the form:

$$\Delta T(m) = -v1.998m - bm^{1.5} - cm^2 \quad (6.15)$$

where m is the molality of the given salt expressed in mol kg^{-1} , and the first coefficient was fixed to the theoretical value $RT_m^2 M_w / \Delta H_m$, evaluated using the values for the melting temperature T_m and the melting enthalpy ΔH_m of the TIP4P/2005 model [49]. The fitted parameters are provided in Table 6.3. Note that for Li_2SO_4 the fit for the simulated data was not included, because the freezing point was calculated for only one salt concentration. As can be seen in Figure 6.5, the agreement between the freezing point depression obtained with the Madrid-2019 model and the experimental data [87, 89, 88] is in general very good for all the salts and at all the concentrations considered (the experimental data is given in the supplementary material of this work). Looking into the results in more detail it can be concluded that for NaCl, MgCl_2 and specially for Li_2SO_4 the freezing point depression is slightly underestimated with respect to the experimental data

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Salt	m_i (mol kg ⁻¹)	T (K)	ΔT (K)	m (mol kg ⁻¹)	t_r (ns)	t_a (ns)
NaCl	1	247	-3	1.19(0.05)	1750	550
	2	243	-7	2.13(0.08)	1500	700
	4	236	-14	4.07(0.08)	1200	500
	4*	236	-14	4.02(0.06)	1400	500
	4 ^b	236	-14	3.92(0.08)	1250	550
	4 ^R	236	-14	4.03(0.08)	1250	550
	6	224	-26	6.24(0.05)	1100	400
KCl	1	247	-3	1.02(0.05)	1250	350
	2	243	-7	2.20(0.05)	1100	400
	4	236	-14	3.98(0.05)	900	300
LiCl	4	220	-30	4.48(0.04)	2100	400
	4	225	-25	4.06(0.05)	1200	400
	4	236	-14	3.30(0.05)	4300	450
	6	200	-35	6.20(0.08)	2400	800
MgCl ₂	2	232.5	-17.5	2.15(0.05)	1050	750
	3	215	-35	3.07(0.02)	1150	400
Li ₂ SO ₄	3	233	-17	3.26(0.05)	1250	450

Table 6.2. Details of the simulations to estimate the freezing point depression at 1 bar. To assess the effect of changing the model parameters between the Madrid-2019 and the Madrid-2017 model for NaCl, the freezing point was estimated at $T = 236$ K using both models (the asterisk indicates that the Madrid-2017 model was used). We checked the possible existence of finite size effects by running a simulation with a bigger system (indicated with a b super-index) and the cut-off effect by running a simulation with a cut-off distance of 12 Å (indicated with a R super-index). Here m_i is the initial concentration of the solution, T is the temperature, m is the average molality at equilibrium, t_r is the time the systems are simulated for, and t_a is the time accounted to average the concentrations. The uncertainty in the average molality was estimated from the standard deviation of the values used to calculate m .

Salt	b	c
NaCl	-1.614	0.6721
KCl	-1.567	0.6663
LiCl	-2.315	1.605
MgCl ₂	-6.859	5.676

Table 6.3. Parameters of the quadratic polynomial fit of the freezing point depression of this work’s simulation results, $\Delta T = T_m^{solution} - T_m$, as a function of the salt concentration m . The function used for the fit is given by $\Delta T(m) = -\nu 1.998 m - b m^{1.5} - c m^2$, where m is the molality of the given salt expressed in mol kg^{-1} and the first coefficient is assigned the theoretical value $RT_m^2 M_w / \Delta H_m = 1.998$, obtained using the values of T_m and ΔH_m for the TIP4P/2005 model and ν , the number of ions per mol of salt.

over the whole salt concentration range. For KCl and LiCl, the agreement with experiments is rather good for all the salt concentrations.

As mentioned before, there are not many simulation studies of the freezing point depression that can be used to compare the performance of the Madrid-2019 model with other model potentials commonly used in electrolyte aqueous solutions. We are only aware of three previous estimates of the freezing point depression of water for NaCl solutions, also obtained by using the direct coexistence method, and which have been included in Figure 6.7 for comparison. The first estimation was performed by Kim and Yethiraj [15] who described water using the TIP5P model, and the Åqvist [92] and OPLS force fields for Na⁺ and Cl⁻, respectively. Note that this model uses integer charges for the ions.

In the work of Soria *et al.* [17] the descent in the melting point for a salt solution at a 2 mol kg^{-1} concentration was estimated using the Joung Cheatham model for NaCl (that was parameterized for SCP/E water and uses integer charges for the ions) and the TIP4P/2005 model for water. This model yields a higher point depression than the Madrid-2019 model, overestimating the experimental result. Conde *et al* [16] performed a more systematic study, covering several salt concentrations up to 4 mol kg^{-1} . In this case, the solution was modelled using also TIP4P/2005 and a model with integer charges for NaCl [93]. The agreement with experiments is comparable to that obtained with the Madrid-2019 model. The difference is that the results of Conde *et al.* slightly overestimate the experimental results, whereas the Madrid-2019 model underestimates them.

Since the Madrid-2019 model modifies the NaCl parameters with respect to a previous model fitted only to properties of this salt (the Madrid-2017 model [48]) so that the same parameters can be used in several saline solutions, it is pertinent to study whether the freezing point depression is affected by this reparametrization. In principle, since the two model potentials are quite similar, it is expected that both will exhibit the same freezing point depression for the NaCl + H₂O system. We checked that this is indeed true by performing additional direct coexistence simulations of the ice-NaCl solution interface at $T = 236 \text{ K}$, close to the experimental eutectic point. As can be seen in Figure 6.7, the value obtained with the

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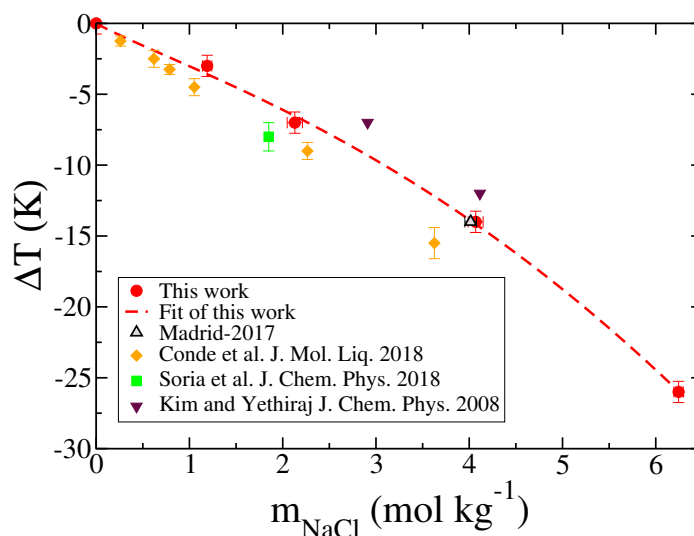


Figure 6.7. Freezing point depression of ice in contact with NaCl aqueous solutions as a function of salt concentration obtained with the Madrid-2019 model, compared to the results for other force fields taken from the literature. The Madrid-2017, Conde *et al.* [16] and Soria *et al.* [17] data were obtained employing force fields that use TIP4P/2005 for water. For this reason they provide the same results at low concentrations where the freezing point depression is a colligative property. However, they differ at moderate and high concentrations due to the different force field used for NaCl that provokes that the curve of activity versus concentration is not identical. Kim and Yethiraj employed a force field that uses TIP5P for water, that predicts a lower value of the constant of proportionality of Eq. 6.11, see Table 6.5. This explains why this model underestimates the freezing point depression. The melting point of pure water for TIP5P was taken as 272 K [66]. The T_m^{solution} taken from Ref. [17] is the one obtained by the chemical potential route, 242 K.

model Madrid-2017 coincides within the statistical uncertainty with that provided by the Madrid-2019 model. Thus, we can conclude that the slight modification of the parameters from the Madrid-2017 to the Madrid-2019 model for NaCl does not change the performance on the estimation of the freezing point depression.

The freezing point depression curves for all the studied salts are gathered in Figure 6.8 (a), together with the experimental data. This figure illustrates that the Madrid-2019 model provides a good overall description of the effect different salts have on the equilibrium ice-solution curves for all the salts and at all concentrations considered. As described in Section 6.3, the freezing point depression if the mixture were ideal can be easily computed from the chemical potentials of ice and water in the pure system, and these results have been included in Figure 6.8 (b) for comparison. Note that there are two ideal curves depending on the number of ions present in the salt (two ions per salt molecule in 1:1 salts and three ions per salt molecule in 2:1 and 1:2 salts). These curves were calculated using the experimental water activity [85], from which it is straightforward to calculate $\Delta\mu^0(\Delta T)/RT$, and solving Eq. 6.12 for different values of the water molar fraction x_{wat} . As can be seen in Fig. 6.8 (b), the freezing point exhibits small deviations from the ideal behaviour (i.e., lower than 0.4 K) for concentrations lower than 1 mol kg⁻¹ for 1:1 electrolytes and for concentrations lower than 0.35 mol kg⁻¹ for 1:2 or 2:1 electrolytes. Above these concentrations deviations from ideal behavior are clearly visible.

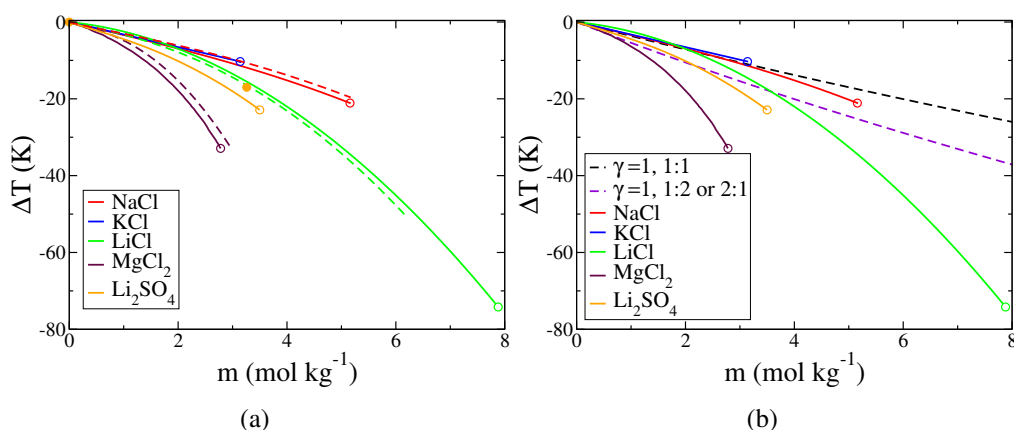


Figure 6.8. Freezing point depression curves for different salty aqueous solutions. (a) Comparison between the experimental data (solid lines) and the simulation results with the Madrid-2019 model (dashed lines). (b) Comparison between the experimental data (solid lines) and the ideal behaviour (dashed lines). The ideal behaviour was calculated using the experimental water activity [85], from which it is straightforward to calculate $\Delta\mu^0(\Delta T)/RT$, and solving Eq. 6.12 for different values of the water molar fraction x_{wat} . The experimental eutectic points are marked with empty circles.

6.5 Discussion

One might think that if the freezing point depression is in good agreement with experiments, this means that the force field should also provide accurate estimates of the activity of water as a function of supercooling and as a function of salt concentration, as well as of the activity of salt (or the salt osmotic coefficient). In what follows we will show that this is not entirely true.

6.5.1 Activity of water as a function of supercooling

The natural logarithm of the water activity as a function of supercooling, $\ln a_{wat}(\Delta T)$, for the TIP4P/2005 model (calculated using Eq. 6.13) is given in Table 6.4 and represented in Figure 6.9, along with experimental data taken from Ref. [85]. As can be seen in Fig. 6.9 (a), the TIP4P/2005 yields results that are in reasonable agreement with experiments, but there is a small deviation as supercooling increases. How can we explain these differences? As given in Ref. [86], the logarithm of the water activity along the freezing curve can be expanded as a polynomial function of ΔT , whose linear term is given by $\Delta H_m/RT_m^2$, where T_m and ΔH_m are, respectively, the melting temperature and the melting enthalpy of pure water. The first term of this expansion is shown in Fig. 6.9 (b) with a dotted line. As can be seen, this term alone already gives a fairly accurate estimation of the water activity, specially in the experimental case in which both lines are practically overlying. For TIP4P/2005, this approximation is also fairly good, but it slightly deteriorates as temperature decreases. From these results, we can conclude that by looking at the value of $\Delta H_m/RT_m^2$, one can get a first indication on whether the water model provides a reasonable estimate of the water activity. The value of this quantity for several popular water models is given in Table 6.5. It seems clear from these data that TIP4P/2005 is the model that gives a better estimation of the water activity, followed by TIP4P/Ice, being TIP5P the one with larger deviations from experiments.

But coming back to the differences between the experimental activity and that predicted by the TIP4P/2005 model, we have just seen that $\Delta H_m/RT_m^2$ explains much, but not all the discrepancy between experiments and the TIP4P/2005 model, specially as temperature decreases. To explain these differences, we resort to the expansion of the chemical potential difference between ice and water: [91]

$$\Delta\mu^0 = \frac{\Delta H_m \Delta T + \Delta C_{p,m} (\Delta T)^2 / 2}{T_m}, \quad (6.16)$$

where $\Delta C_{p,m}$ is the difference between the heat capacity at constant pressure of pure water and ice at the melting point of pure water. Eq. 6.16 can be obtained from the chemical potential difference between ice and water that is obtained when $\Delta C_{p,m}$ is assumed to remain constant [94]:

$$\Delta\mu^0 = \Delta H_m \left(\frac{T}{T_m} - 1 \right) + \Delta C_{p,m} T \left[\frac{T_m}{T} - 1 - \ln \left(\frac{T_m}{T} \right) \right] \quad (6.17)$$

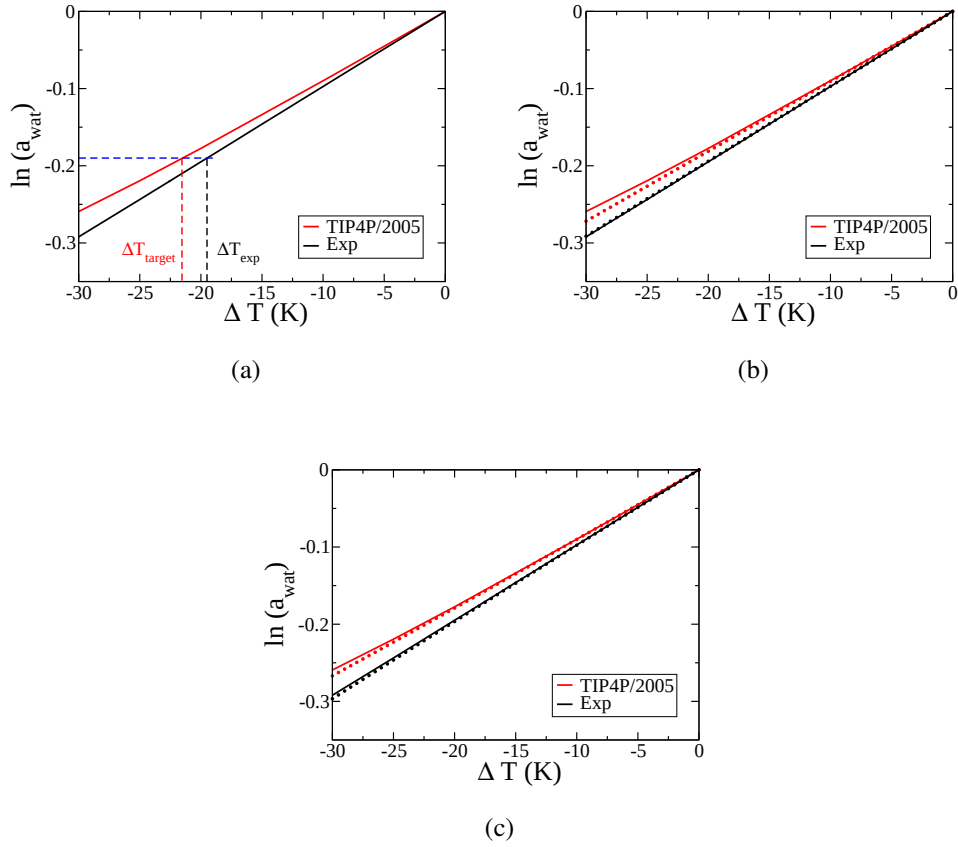


Figure 6.9. (a) Comparison of the natural logarithm of the water activity as a function of the freezing point depression for the TIP4P/2005 water model (red line) and from experiments taken from Ref. [85] (black line). (b) and (c) The natural logarithm of the water activity is compared with (b) an estimate obtained from the first term of the expansion taken from Ref. [86], which is given by $(\Delta H_m/RT_m^2)\Delta T$, and (c) with that obtained using the two terms of the expansion given in Ref. [91]. In both figures, solid lines are the exact values and the dotted lines the estimates from the expansions.

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Salt	m (mol kg ⁻¹)	$T_m^{solution}$ (K)	$\frac{\Delta\mu^0}{RT_m^{solution}}$	a_{wat}	γ_{wat}
NaCl	2	244.06	-0.054	0.948	0.982
	3	240.26	-0.088	0.916	0.966
	4	235.91	-0.126	0.881	0.945
	6	225.54	-0.215	0.807	0.894
KCl	2	243.72	-0.057	0.945	0.979
	3	240.01	-0.090	0.914	0.963
	4	235.91	-0.126	0.881	0.945
LiCl	2	242.83	-0.065	0.937	0.971
	3	235.95	-0.126	0.882	0.929
	4	226.89	-0.204	0.816	0.874
	6	202.19	-0.385	0.680	0.754
MgCl ₂	2	234.78	-0.136	0.873	0.904
	3	216.54	-0.286	0.752	0.792

Table 6.4. Water activities (a_{wat}) and activity coefficients (γ_{wat}) for the different salts along the freezing depression curve. $\Delta\mu^0(T_m^{solution})$ is the chemical potential difference between ice and pure water at the freezing point of the considered solution.

This equation is exact (within the $\Delta C_p = \Delta C_{p,m}$ approximation). Substituting T by $T_m + \Delta T$ in Eq. 6.17 and doing a Taylor expansion with respect to ΔT , one arrives to Eq. 6.16. Thus, Eq. 6.16 is approximate, whereas Eq. 6.17 is exact (within the $\Delta C_p = \Delta C_{p,m}$ approximation).

From Eq. 6.13 it follows that $\Delta\mu^0 = RT \ln(a_{wat})$. The heat capacities of ice and water at melting of TIP4P/2005 were taken from Ref. [95], whose values are $C_{p,ice}(T = 250 \text{ K}) = 13.890 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $C_{p,wat}(T = 250 \text{ K}) = 24.058 \text{ cal mol}^{-1} \text{ K}^{-1}$. For the experiments we used $C_{p,ice}(T = 273 \text{ K}) = 9.015 \text{ cal mol}^{-1} \text{ K}^{-1}$ [96] and $C_{p,wat}(T = 273 \text{ K}) = 18.013 \text{ cal mol}^{-1} \text{ K}^{-1}$ [97]. The $\ln(a_{wat})$ estimated from this route is compared with the exact value in Fig. 6.9(c) and now both the experimental activity and that predicted with TIP4P/2005 are practically coincident with that obtained from Eq. 6.16 (using, respectively, the experimental and simulated enthalpy of fusion and the heat capacity change at melting). Thus, although the value of the term $\Delta H_m / RT_m^2$ is enough to understand qualitatively the differences between experiments and simulations, the change of heat capacity at melting must also be taken into account to fully understand the discrepancies. Note that $\Delta C_{p,m}$ adopts fairly similar values in experiments ($\Delta C_{p,m} = 8.998 \text{ cal mol}^{-1} \text{ K}^{-1}$) and in the TIP4P/2005 model ($\Delta C_{p,m} = 10.168 \text{ cal mol}^{-1} \text{ K}^{-1}$), but the slope of the heat capacity of ice is not well reproduced by classical simulations, as this property is significantly affected by nuclear quantum effects that must be explicitly incorporated in the simulations [95].

Model	T_m (K)	ΔH_m (kcal mol ⁻¹)	$\Delta H_m/RT_m^2$ ($\times 10^3$ K ⁻¹)	$RT_m^2 M_w/\Delta H_m$ (K kg mol ⁻¹)
TIP4P/2005	250	1.125	9.06	1.998
TIP4P/Ice	270	1.29	8.80	2.048
TIP5P	272	1.75	11.90	1.514
Exp	273.15	1.44	9.71	1.856

Table 6.5. Evaluation of the factor $\Delta H_m/RT_m^2$ for pure water that provides the linear coefficient of a polynomial expansion of $\ln a_{wat}$ as a function of the freezing point depression ΔT , for different water models typically used to study salt solutions, together with the experimental value. Data for TIP4P/2005 was taken from Ref. [49], for TIP4P/ice from Ref. [69] and for TIP5P from Ref. [64]. The last coefficient of the Table yields the coefficient of the freezing point depression of an ideal solution (see Eq. 6.11 of the main text).

6.5.2 Osmotic coefficient as a function of salt concentration

Another condition that the force field should fulfill to reproduce the freezing point depression is that it should describe how the activity of water changes with the concentration of salt. This last dependence is captured by the osmotic pressure, i.e. the pressure at which a solution and the solvent separated by a semipermeable membrane are in equilibrium. Related with the osmotic pressure, one can also measure the osmotic coefficient that can be calculated using the Lewis-Randall definition:

$$\phi(T, p, m) = -\frac{\ln a_{wat}(T, p, m)}{\nu m M_{wat}} \quad (6.18)$$

where ν is the number of ions that result from the dissociation of a salt molecule. In the literature, it is common to find the variation of the osmotic coefficient with the salt concentration at constant temperature and pressure. However, the present simulations do not provide enough information to construct the whole activity curve as a function of both temperature and salt concentration. But if we combine the activity of water as a function of supercooling, $a_{wat}(\Delta T)$, and the freezing point depression as a function of the salt concentration, $\Delta T(m)$, we can estimate the osmotic coefficient of the salt along the freezing curve. Note that $a_{wat}(\Delta T)$ is a universal curve for all the salts [4], but $\Delta T(m)$ is different for each salt.

As can be seen in Figure 6.10, the osmotic coefficient shows only a mild dependence with temperature. The experimental data at 273 K and 298 K are fairly close to each other [98]. Coherently with this observation, the osmotic coefficient along the freezing depression curve, obtained from the Lewis-Randall expression in conjunction with the experimental data for $a_{wat}(\Delta T)$ from Ref. [85] and $\Delta T(m)$ from Ref. [89], is in good agreement with the curves at constant temperature from Ref. [98], specially with that at $T = 273$ K up to 3 mol kg^{-1} . Thus, we can conclude that the osmotic coefficient calculated at the freezing depression curves gives a reasonable estimate of the osmotic coefficient at 273 K.

Once we confirmed that the osmotic coefficient only exhibits a small dependence with temperature, we again used the Lewis-Randall expression but now with the data obtained from simulations with the Madrid-2019 model for $a_{wat}(\Delta T)$ and $\Delta T(m)$. The results are shown in Fig. 6.10 (b), together with the osmotic coefficient for other force fields at 298 K taken from Ref. [7]. The Madrid-2019 model underestimates the osmotic coefficient up to about a 20%, but the predicted curve runs almost parallel to the experimental one above a 1 mol kg^{-1} concentration. We have included in Figure 6.10 (b) the osmotic coefficient evaluated using the larger system. Although its value is slightly closer to the experimental one, the deviation is still large showing that finite size effects are not responsible for the deviation between experimental and the value of the osmotic coefficient predicted by the Madrid-2019 force field. The osmotic coefficient is related to the variation of the chemical potential of water when salt is added.

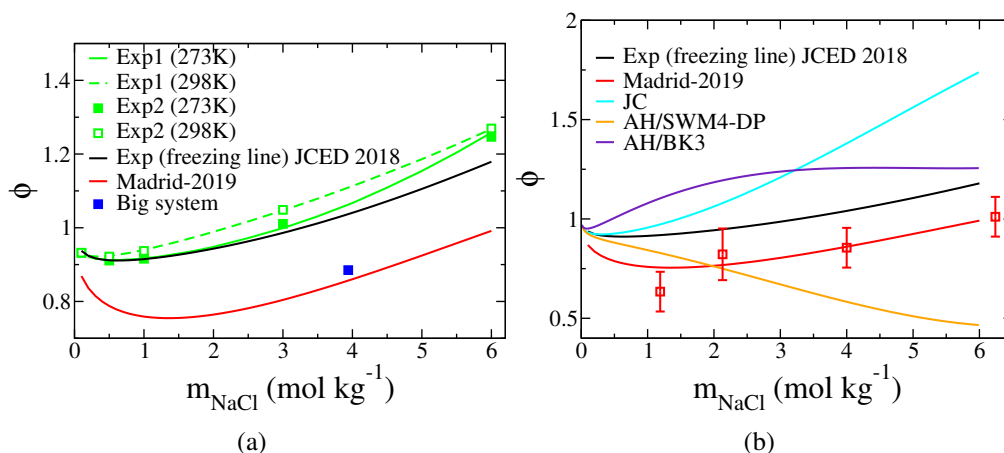


Figure 6.10. Osmotic coefficient of a NaCl solution. (a) Experimental data at $T = 273\text{ K}$ and $T = 298\text{ K}$ from two different sources (Exp1 from Ref. [98] and Exp2 from Ref. [99]) are shown in green lines, finding an excellent agreement between both sets of data. The estimate obtained from the Lewis-Randall expression using the experimental data ($a_{\text{wat}}(\Delta T)$ from Ref. [85] and $\Delta T(m)$ from Ref. [89]) is designated as Exp (freezing line) JCED 2018. The results provided by the Madrid-2019 model are also shown. (b) The osmotic coefficients for other electrolyte models (at $T = 298\text{ K}$ taken from Ref. [7]) are compared with the Madrid-2019 model and experimental data. JC stands for the non-polarizable Joung–Cheatham force field tailored to SPC/E water [22]. AH/SWM4-DP [100] and AH/BK3 [101] are both aqueous alkali halide force fields tailored to the polarizable models of water SWM4-DP [102] and BK3 [103]. For the Madrid-2019 model, besides the results obtained from the fit, the data calculated from the freezing point depressions given in Table 6.2 are also shown.

The osmotic coefficients of the other force fields included in Fig. 6.10 exhibit even larger departures from experiment, failing to reproduce the correct dependence with salt concentration. This includes the popular Joung–Cheatham force field (that uses SCP/E for water) and two polarizable force fields, all with integer charges. These models correctly predict the osmotic coefficient at low concentrations but fail to capture the dependence with salt concentration. Thus, it seems that although the Madrid-2019 model does not give the correct absolute value (due to the use of scaled charges), it provides the best dependence with concentration.

6.5.3 Freezing point depression

In the two preceding sections we have seen that the Madrid-2019 model does not give an accurate description of either the water activity or the osmotic coefficient, so how is it possible that this model gives a reasonable description of the freezing point depression? The reason is that there is a cancellation of errors between the water activity and the salt osmotic coefficient. The overestimation of the water

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activity of the TIP4P/2005 model is compensated by the description of the impact of adding salt to the solution.

6.5.4 Target freezing point depression

Now that we have better understood what the contributions of the water activity and the salt osmotic coefficient to the estimation of the freezing point depression are, it is pertinent to analyze what the desired behaviour for a good model of electrolyte solutions should be. As we have just seen, some of the deficiencies of the electrolytes force fields describing the freezing point depression arise from deficiencies of the considered water model to reproduce the water activity. The changes in the chemical potential of salt and the activity of water are related by the Gibbs-Duhem relation (Eq. 6.14). If a force field correctly reproduced the water activity for any value of m , that means that it would also reproduce the osmotic coefficient and the activity coefficient of the salt, as the osmotic coefficient and the $\ln \gamma$ are related to each other at constant temperature and pressure [84]. Making the approximation that the changes in the osmotic coefficient (and, consequently, in the logarithm of the activity coefficient of the salt, $\ln \gamma$) with temperature at constant composition are small, we can calculate the target freezing point in the following way. First, for a given salt molality, m , we look for the experimental freezing point depression (ΔT_{exp} in Fig. 6.9 (a)). Second, for this value of ΔT_{exp} , we look for the experimental value of $\ln a_{wat}$ (Fig. 6.9 (a)). And third, we see for which ΔT the water model gives the experimental $\ln a_{wat}$, and this would be the target freezing point depression ΔT_{target} for molality m (Fig. 6.9 (a)). In this way, we are subtracting the inherent error coming from the inability of the water model to give the right values of the water activity. This target curve is approximate, since it was obtained by disregarding the variation of ϕ or $\ln \gamma$ with temperature. However, as can be seen by comparing the experimental osmotic coefficient of NaCl along the freezing curve and at $T = 273$ K shown in Fig. 6.10 (a), this is a fairly good approximation up to 4 mol kg^{-1} , and reasonable beyond that concentration. The target freezing depression curve for NaCl using the TIP4P/2005 model for water is given in Fig. 6.11. If we want to have a model for NaCl solutions using TIP4P/2005 that correctly describes the salt osmotic coefficient, we should aim to reproduce this target curve, rather than the true experimental one. In this case, when fitting or testing the model parameters one should aim to over-estimate the freezing point depression following the target curve. Note that this curve is universal for any NaCl solution model that uses TIP4P/2005 to describe water. Similar target curves have been estimated for other salts (KCl in Fig. 6.11 (b) and LiCl in Fig. 6.11 (c)). Note that the larger departures of the target from the experimental curve are observed for LiCl, as this salt is the one for which the eutectic point appears at higher salt concentrations.

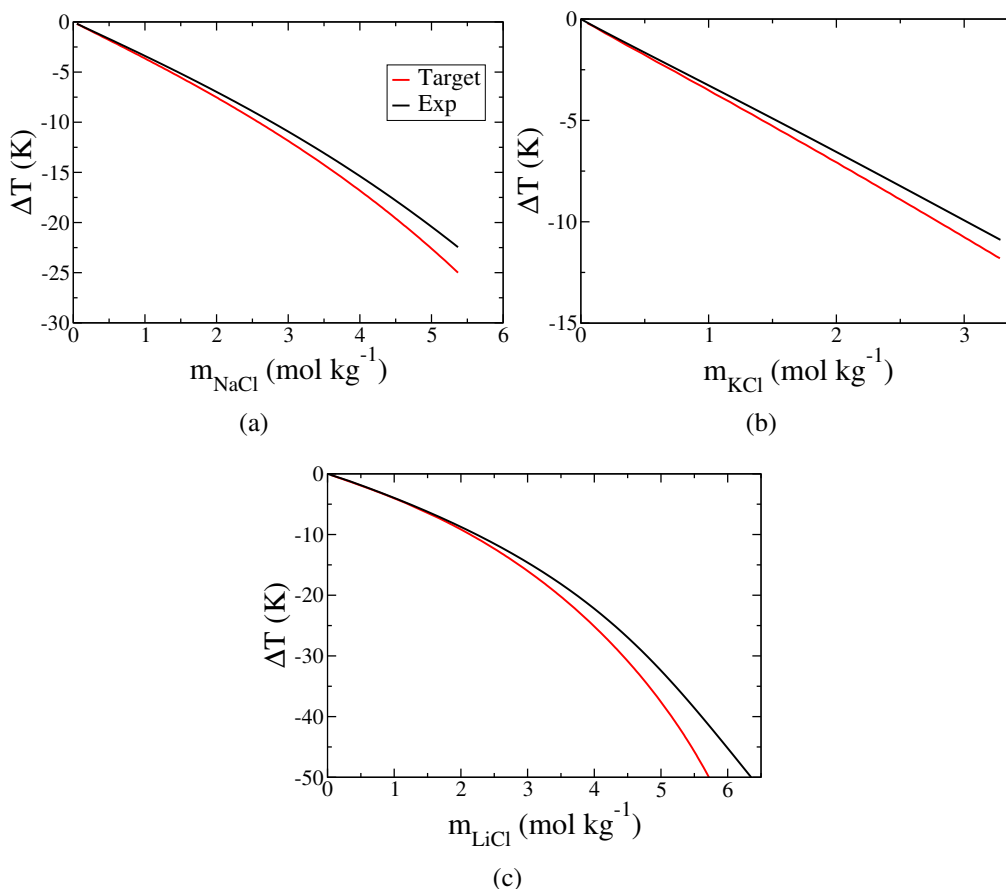


Figure 6.11. Target freezing point depression curves for the NaCl (a), KCl (b) and LiCl (c) solutions for a model that reproduces properly the change of the activity of water as a function of the salt concentration. These curves take into account that the TIP4P/2005 model does not correctly reproduce the activity of water as a function of supercooling.

6.6 Conclusions

In this work we have shown that the Madrid-2019 model provides a faithful description of the experimental freezing point depression of five salt solutions (NaCl, KCl, LiCl, MgCl_2 and Li_2SO_4) at concentrations up to the eutectic point. The best agreement is obtained for KCl and LiCl, whereas the freezing point depression of NaCl, MgCl_2 , and Li_2SO_4 , are slightly underestimated over the whole concentration range that covers up to the eutectic point. By analyzing the possible causes of the differences between the simulated and experimental data, we discovered that the water model TIP4P/2005 introduces some error in the water activity along the freezing curve. Thus, when fitting or testing the goodness of an electrolyte model, it is wise not to try to reproduce the experimental freezing point, but rather one should target a freezing depression curve obtained by subtracting the error introduced by the use of a water model that does not reproduce exactly the activity of

6. Freezing point depression of salt aqueous solutions using the Madrid-2019 model

water. Otherwise, the electrolyte model can only provide an accurate estimation of the freezing point depression by a cancellation of errors between the description of the water activity and the salt osmotic coefficient. We have also seen that the Madrid-2019 model underestimated the osmotic coefficient of NaCl over the whole concentration range, but at molalities higher than 1 mol kg^{-1} , the simulated and experimental curves run parallel to each other. This underestimation of the osmotic coefficient compensates to some extent the higher activity of water of the TIP4P/2005 model for a certain supercooling, thus yielding reasonable freezing curves due to a certain cancellation of errors. In the future it would be of interest to check the performance of other force fields of electrolytes for predicting the freezing point depression. Notice that reproducing the freezing point depression without cancellation of errors would require a water model with the right melting temperature and melting enthalpy and a force field of ions able to reproduce the osmotic coefficient up to high concentrations for temperatures well below the melting temperature of pure water. Certainly a force field like that has not been proposed so far. The Madrid-2019 force field, is far from being perfect but it does a reasonable job in describing the experimental results. This adds to number of properties whose description improves with the Madrid-2019 model as compared to other non-polarizable models with integer charges, that include the densities, viscosities and diffusion coefficients of salt solutions at atmospheric conditions and up to the solubility limit [33], and even the solubility limit of NaCl [48]. The trade off is that these type of potentials are not adequate to describe properties of pure salts [8, 57] (either in solid or liquid state), in which the charge distribution of the ions is expected to be very different from that in aqueous solution.

We hope the freezing point depression becomes a standard property to be tested when proposing force fields for electrolytes as its determination is relatively straightforward and feasible with current computational resources. Besides it provides easy and straightforward information about the osmotic coefficient electrolyte solutions. The osmotic coefficient is calculated right the way, although certainly not along an isotherm but along the coexistence curve.

6.7 Acknowledgments

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Homogeneous nucleation of NaCl in supersaturated solutions

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7.1 Abstract

The Seeding method is an approximate approach to investigate nucleation that combines molecular dynamics simulations with classical nucleation theory. This technique has been successfully implemented in a broad range of nucleation studies in the recent years. However, its accuracy is subject to the arbitrary choice of the order parameter threshold used to distinguish liquid-like from solid-like molecules. We revisit here the crystallization of NaCl from a supersaturated brine solution and show that consistency between Seeding and rigorous methods like Forward Flux Sampling (from previous work) or spontaneous crystallization (from this work), is achieved by following a mislabelling criterion to select such threshold (i.e. equaling the fraction of mislabelled particles in the bulk parent and nucleating phases). This work supports the use of Seeding to obtain fast and reasonably accurate nucleation rate estimates and the mislabelling criterion as one giving the relevant cluster size for classical nucleation theory in crystallization studies.

7.2 Introduction

Crystallization from a pure liquid is usually viewed as a two step process in which homogeneous nucleation precedes growth. The crystal nucleus that determines the end of nucleation and the beginning of growth is the critical one [1, 2]. This state corresponds to the top of the free energy barrier between the supercooled liquid and the solid which appears due to the energetic penalty of forming a new interface. In the absence of surfaces or impurities, the free energy barrier is only overcome by thermal fluctuations, which makes this process a rare event. Moreover, the typical size and lifetime of a critical nucleus are $\sim$ nm and $\sim$ ns respectively. Thus, studying nucleation is like trying to find a needle in a haystack both in a spacial and in a temporal sense [3].

Computer simulation has become a valuable tool for studying nucleation because it has access to the relevant length scale [4, 5, 6]. However, the time disparity between nucleus lifetime and nucleation occurrence makes it necessary to use special rare event methods. Some examples are transition path sampling (TPS) [7, 8], forward flux sampling (FFS) [9, 10] or metadynamics [11, 12, 13]. Although rigorous, these methods are computationally expensive [14].

Seeding is a less expensive but approximate approach in which the simulation starts with a fluid in which a crystal nucleus has been inserted [15, 16, 17]. Seeding exploits the fact that the critical nucleus is a state of unstable equilibrium. Under isobaric-isothermal (NpT) conditions, a critical cluster in the top of the free energy barrier has fifty percent chances of either dissolving or growing towards the crystallization of the whole system. Thus, by inserting a crystal seed inside of a pre-equilibrated metastable liquid and then following the time evolution of the size of the crystal seed, one can estimate the critical size at the conditions of interest. The size of the critical cluster obtained in such simulations, alongside other properties of the bulk liquid and crystal phases, are plugged into the Classical Nucleation Theory (CNT) formalism [18, 19, 20, 21] to get relatively inexpensive estimates of nucleation parameters such as the nucleation rate, the height of the nucleation free energy barrier or the surface tension.

However, the main drawback of Seeding is the arbitrariness with which the nucleus size is determined. It has been recently shown that different ways to obtain the number of particles belonging to the solid nucleus may lead to discrepancies of several orders of magnitude in the nucleation rate of NaCl from a supersaturated brine [22], which is a quite discouraging result for current or potential Seeding users [23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40]. In this work we revisit this problem and show that when the order parameter threshold to identify particles belonging to the crystal nucleus is tuned with the mislabelling criterion [41] (i.e. equal number of mislabelled particles in the liquid and the solid bulk phases), Seeding can give nucleation rates consistent with those obtained by methods that do not depend on an order parameter, such as Forward Flux Sampling or spontaneous nucleation [41]. Thus, the nucleation of NaCl from supersaturated brine adds up to the list of systems for which crystal nucleation has been suc-

cessfully investigated with Seeding in conjunction with the mislabelling criterion: hard spheres [41, 42, 43], Lennard-Jones [41], NaCl from its melt [44], ice from pure water [17, 45, 46, 47, 48], ice from brine [49, 50] and oppositely charged colloids [51]. Therefore, although Seeding does strongly depend on the order parameter, it seems to work for a wide range of systems when the mislabelling criterion is employed to tune the order parameter.

7.3 Model and simulation details

We use the JC/SPC/E force field which uses +1 and -1 charges plus a Lennard-Jones potential for the ions and the nonpolarizable SPC/E water model [52]. The solubility of this model has been widely studied, reaching a consensual value of approximately 3.7 mol kg^{-1} [53, 54, 55, 56] at 1 bar and 298.15 K. Moreover, there are nucleation rate estimates obtained via FFS to compare with [10].

We shall compute nucleation rates for solutions of molality 8, 10, and 12 mol kg^{-1} using Seeding. Furthermore, we shall compute nucleation rates for high concentrations via brute force runs of metastable NaCl solutions for molalities ranging from 14 to 15 mol kg^{-1} allowing us to check how our Seeding results extrapolate to such regime.

Molecular Dynamics simulations are performed with the GROMACS package 2016.4 [57]. We use Parrinello-Rahman barostat [58] to maintain the system at 1 bar, with a relaxation time of 2 ps and a compressibility of 10^{-5} bar^{-1} . To control the temperature and keep it at 298.15 K we use Nosé–Hoover thermostat [59] with a relaxation time of 2 ps. For the Verlet integration of the equations of motion, we use a time step of 2 fs. To deal with electrostatic interactions we use particle mesh Ewald summations [60]. The cut-off radius for the neighbour list, the dispersive and electrostatic interactions is $9 \text{ \AA}$. The LINCS algorithm is used to fix the geometry of the water molecules, with an order of 6 and 4 iterations [61, 62].

For the seeding simulations, boxes are cubic and the edge length is approximately $L \approx 8.3 \text{ nm}$ and contain nearly 15000 water molecules and the corresponding number of ions (between 4000 and 6600 ions depending on the concentration and the size of the inserted seed).

When using Seeding, we need to compute the number of ions in the solid cluster (see the following section). To label ions as solid-like or solution-like we use a modified version of the $\bar{q}_4$ parameter proposed by Lechner and Dellago [63], which we compute with a cut-off radius of $4 \text{ \AA}$. Notice that water is not included in the evaluation of the order parameter and cations and anions are treated as identical particles. The introduced modification is that we do not divide in Eq. (6) of Ref. [63] by $\tilde{N}_b$, the number of neighbors plus 1. As can be seen in Fig. 7.1 (b), the usual normalized $\bar{q}_{4,n}$ is not able to distinguish solid-like from solution-like atoms, because the probability distributions of $\bar{q}_{4,n}$ in the solutions overlap completely with that of the solid, a problem that is solved by removing the normalization. The unnormalized $\bar{q}_4$, instead, separates nicely solid-like from

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solution-like atoms (Fig. 7.1 (a)). This modification is recommended for problems regarding precipitation of salts from solution.

We use the mislabelling criterion [41] to set the threshold value, $\bar{q}_{4,t}$, above which a particle is considered to belong to the solid phase. Such criterion consists in finding the $\bar{q}_{4,t}$ value for which the fraction of mislabelled particles in the bulk solid is equal to that of the bulk solution. To find such threshold, we first run a simulation of the bulk solid and gather 1000 configurations of 1000 ions each. With these configurations we work out, for a given $\bar{q}_{4,t}$ value, the fraction of ions that are not labelled as solid (mislabelled particles). This calculation is repeated for the same set of configurations and different values of $\bar{q}_{4,t}$ until we get the black curve given in Fig. 7.1. Such curve monotonously increases because the fraction of ions which are not detected as belonging to the solid increases as we increase $\bar{q}_{4,t}$. We do the same with the solution. We run a bulk solution simulation and gather 1000 independent configurations. Then, we compute the fraction of ions that are detected as solid-like in such configurations for a series of $\bar{q}_{4,t}$ values and we obtain the red, green and blue curves for 8, 10 and 12 mol kg⁻¹ solutions respectively (the ionic concentration is given in molality, or mol of NaCl per kg of water). When computing these curves we did not take into consideration isolated ions with no neighbors. We have checked, however, that if we had considered these ions as belonging to the solution the curves presented in the figure would have not changed much and the crossing point between the solid and the solution mislabelling curves would remain almost unchanged. The solution mislabelling functions decay monotonously because the fraction of particles labelled as solid-like in the solution decreases when $\bar{q}_{4,t}$ increases. As can be seen in Fig. 7.1, the solid and the three solution curves cross at 3.06 (the concentration barely affects the crossing point). Therefore, for the three concentrations, particles with $\bar{q}_4 > 3.06$ are considered solid-like and particles with $\bar{q}_4 < 3.06$ are considered to belong to the solution. Two solid-like particles are considered neighbors (thus belonging to the same cluster) if they are closer than 4 Å to each other.

Although one might think that by removing the normalization we might be artificially considering as solid-like solution ions with many neighbours belonging to disordered aggregates, the plot of $\bar{q}_4$ versus the number of neighbours shown in Fig. 7.1 (d) indicates that atoms in the solution with three or more neighbours most often adopt low values, rarely reaching values above the threshold. This graph clearly shows that by choosing not to normalize the order parameter, only particles with at least three neighbours can have larger values than the chosen threshold $\bar{q}_{4,t} = 3.06$, i.e., isolated dimers and trimers are always considered solution-like with this order parameter. Note also that atoms with three or more neighbours can adopt values larger than $\bar{q}_{4,t}$, but, as shown in panel c), the probability of mislabelled particles for the chosen $\bar{q}_{4,t}$ is only about 0.1%. In summary, particles need to have at least three neighbours that, besides, need to be oriented properly to attain larger values of $\bar{q}_4$ than $\bar{q}_{4,t}$, so that the probability that the order parameter classifies disordered aggregates as solid is very low, as seen in panel c).

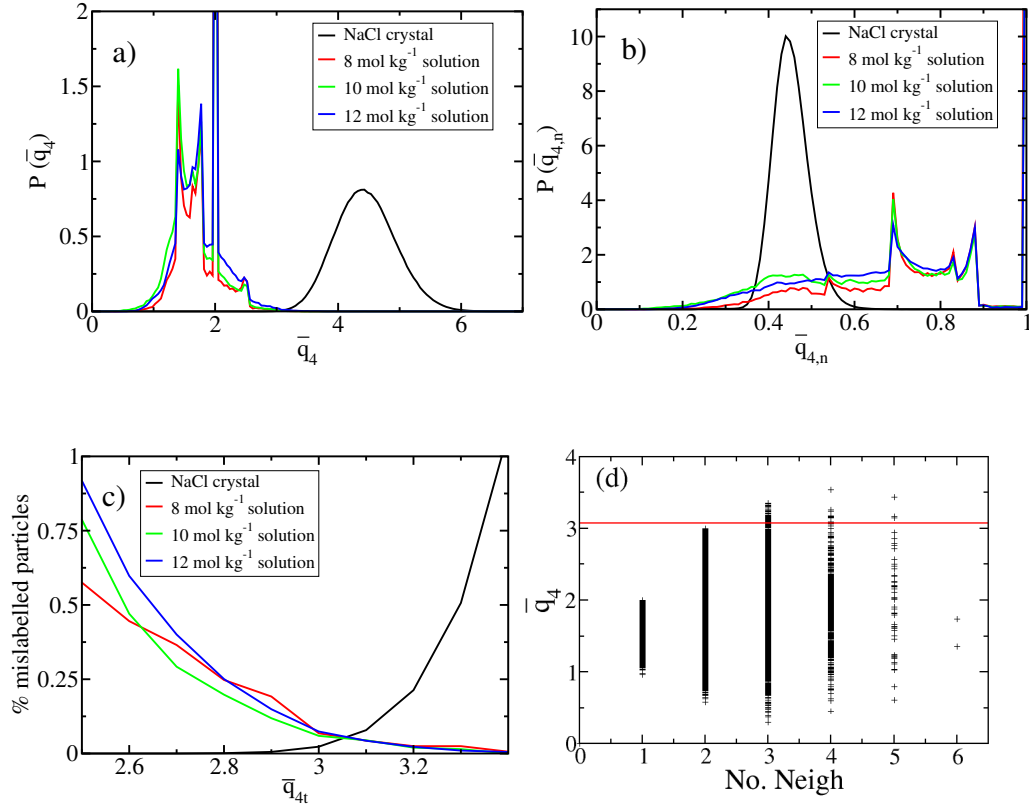


Figure 7.1. Probability distributions of the order parameter $\bar{q}_4$ for the NaCl crystal (black curve), and 8 mol kg⁻¹ (red curve), 10 mol kg⁻¹ (green curve) and 12 mol kg⁻¹ (blue curve) NaCl solutions at 1 bar and 298.15 K, both in a) the unnormalized ($\bar{q}_4$, the one used in this work) and b) the normalized ($\bar{q}_{4,n}$) versions of the order parameter. Note that the probability distribution functions of the normalized version completely overlap with that of the solid, making this order parameter unsuitable to distinguish atoms within solid environments from atoms within solution environments. This problem is solved if the order parameter is not normalized, as in a). c) Percentage of mislabelled particles for the NaCl crystal, and 8 mol kg⁻¹, 10 mol kg⁻¹ and 12 mol kg⁻¹ NaCl solutions as a function of the chosen $\bar{q}_4$ threshold to discriminate between solid and solution-like ions. d) Correlation between $\bar{q}_4$ and the number of neighbours measured in the 8 mol kg⁻¹ NaCl solution.

7.4 Results

7.4.1 Nucleation rate via Seeding

Here, we combine molecular dynamics simulations with CNT to get an approximation of the nucleation rate of NaCl crystals in supersaturated aqueous solutions. According to CNT the free energy barrier height is given by:

$$\Delta G = N_c |\Delta\mu| / 2 \quad (7.1)$$

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where N_c is the number of ions in the critical cluster and $|\Delta\mu|$ is the chemical potential difference per ion between the solid and the solution at the temperature and pressure where the study is carried out. We use the $|\Delta\mu|$ values presented by Zimmermann *et al.* [22] (same ones Jiang *et al.* [10] employed).

To estimate N_c , we first build systems which have a NaCl crystal seed by inserting a spherical cluster cut from the equilibrium NaCl crystal phase in the corresponding solution. We investigate systems with the following solution concentrations: 8 mol kg⁻¹, 10 mol kg⁻¹, and 12 mol kg⁻¹. For each concentration we generate systems with different cluster sizes. We then run simulations and monitor the size of the inserted seed (see Fig. 7.2). As can be seen in Figure 7.2, the lower the concentration, the longer it takes for the cluster to either grow or redissolve.

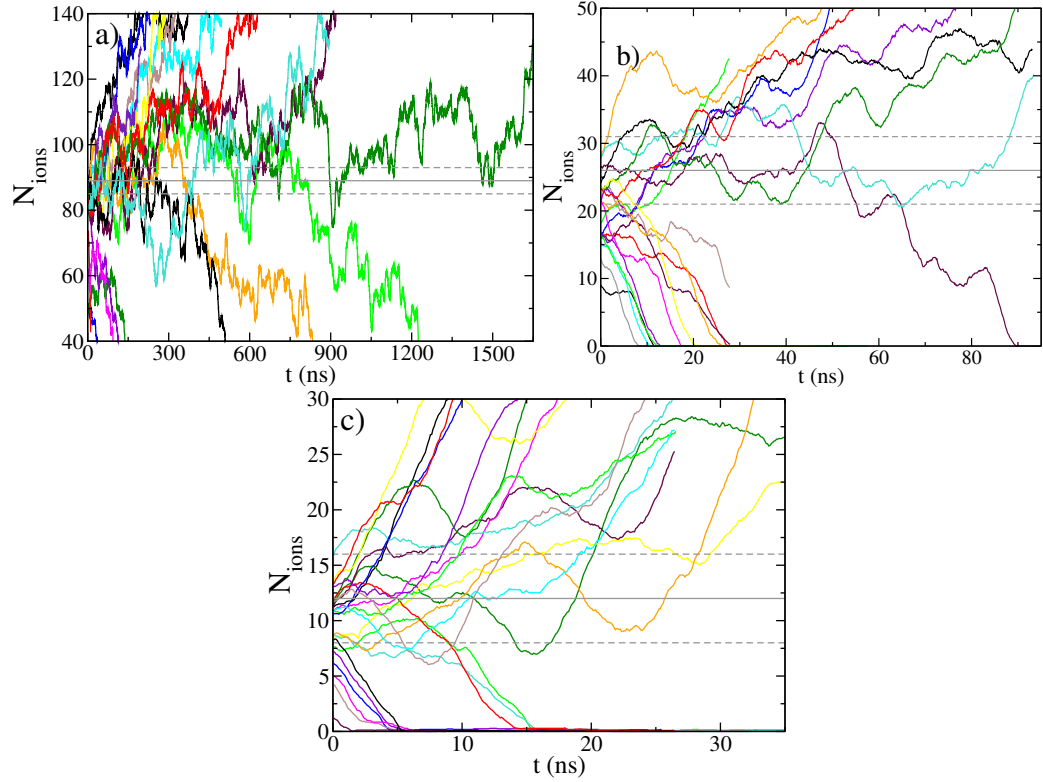


Figure 7.2. Number of particles in the NaCl crystal cluster versus time for different starting configurations in which a NaCl crystal was inserted in a NaCl aqueous solution (at a) 8 mol kg⁻¹, b) 10 mol kg⁻¹, and c) 12 mol kg⁻¹ at $T = 298.15$ K and $p = 1$ bar).

To quantitatively determine the critical cluster size, N_c , we count the number of times that the trajectories shown in Fig. 7.2 experience across a given cluster size N_{ions} . We refer to such number of times as $N_{recrossing}(N_{ions})$. We expect that the trajectories can go back and forth most easily across N_c because the free energy slope is zero at such cluster size. Accordingly, we identify N_c with the position of the maximum in $N_{recrossing}(N_{ions})$. To count $N_{recrossing}$ we do not take into account

the first time a trajectory crosses a given N_{ions} . In this way, the trajectories where the cluster monotonously grows or shrinks do not count in our $N_{recrossing}$ statistics. Fig. 7.3 shows $N_{recrossing}$ vs N_{ions} for the three studied concentrations. From the maxima of such plots we conclude that the critical clusters contain around 89, 26, and 12 ions for the 8 mol kg⁻¹, 10 mol kg⁻¹, and 12 mol kg⁻¹ solutions respectively. It is evident from Fig. 7.3 that the larger N_c the higher is the number of recrossing. This is consistent with the fact that a wider barrier top is expected for higher free energy barriers (or larger N_c).

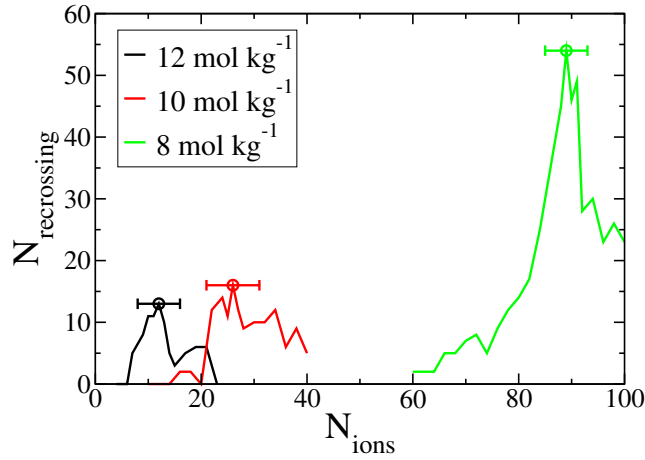


Figure 7.3. Number of recrossing vs. number of particles in the cluster in NaCl solutions at 8 mol kg⁻¹, 10 mol kg⁻¹, and 12 mol kg⁻¹. These results have been obtained from Fig. 7.2.

The CNT equation that we use to calculate the nucleation rate is

$$J = K \exp(-\Delta G/(k_B T)), \quad (7.2)$$

where the kinetic constant K is obtained using the following expression:

$$K = \rho_{ions} D Z, \quad (7.3)$$

where ρ_{ions} is the density of ions in solution and D is the attachment frequency, which we estimate in two different ways. On the one hand, D has been shown to be desolvation limited and to obey the following expression [6, 22]:

$$D_{des} = 4\pi R^2 k_s \sigma_s \rho_{ions}, \quad (7.4)$$

the product of k_s (a second order rate constant) and σ_s (the surface concentration of attachment sites) is only weakly dependent on the nucleus size and is estimated to be 0.066 ms⁻¹ by Zimmermann *et al.* [22]. This value, alongside Eq. 7.4, allows us to do the D_{des} estimates reported in Table 7.1. On the other hand, we use the Auer and Frenkel approach to estimate the attachment frequency as [64]:

$$D_{AF} = \langle (N_{ions}(t) - N_{ions}(0))^2 \rangle / (2t), \quad (7.5)$$

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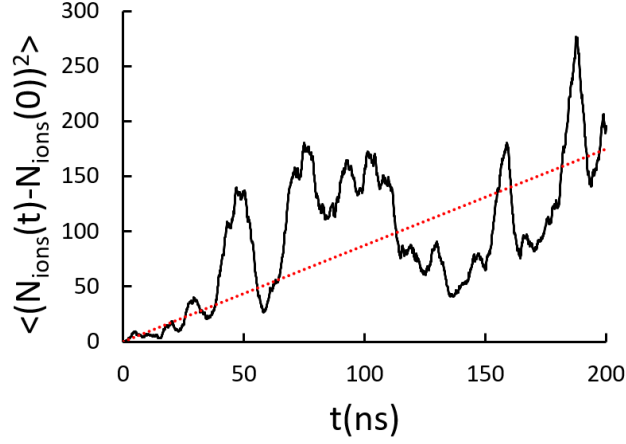


Figure 7.4. Mean squared displacement of the cluster size averaged over three trajectories at 8 mol kg^{-1} where the cluster fluctuates around its critical size

which requires evaluating the slope of the mean squared displacement of the cluster size. In Fig. 7.4 we show in black such mean squared displacement averaged over three of the trajectories in Fig. 7.2(a) while the cluster fluctuates around its critical size. The slope of the linear fit shown in red in Fig. 7.4 divided by two gives an estimate of D , reported as D_{AF} in Table 7.1. We acknowledge that the slope in Fig. 7.4 is quite noisy. However, for all three studied concentrations we get values of the attachment rate of the order of 10^8 - 10^9 s^{-1} , which gives us confidence that we are capturing the right order of magnitude in our calculations. Moreover, also for all three concentrations, D_{des} and D_{AF} are within the same order magnitude, which is quite satisfactory when dealing with nucleation rates. The agreement between theory and simulation gives us further confidence that we are capturing the correct order of magnitude of the attachment rate. We use the D_{AF} values to obtain the nucleation rate given that the Auer and Frenkel approach is a more direct simulation –as opposed to theoretical– estimate of the attachment rate.

R is the radius of the critical nucleus:

$$R = \sqrt[3]{3N_c / (\rho_{solid} 4\pi)}, \quad (7.6)$$

where ρ_{solid} is the density of ions in the NaCl solid at 1 bar and 298.15 K: $\rho_{solid} = 41.445 \text{ nm}^{-3}$. The assumption that the critical clusters are spherical has been supported by Espinosa *et al.*, who compared cubic and spherical NaCl clusters in a Seeding study [44]. In any case, our results are not strongly affected by such an assumption given that: (i) Eq. 7.1, that gives ΔG_c , is valid both for spherical and cubic shapes; and (ii) the kinetic pre-factor does not even change by an order of magnitude from one shape to another.

Finally, Z is the Zeldovich factor [1, 17] is given by:

$$Z = \sqrt{|\Delta\mu| / (6\pi k_B T N_c)}. \quad (7.7)$$

$m/(\text{mol kg}^{-1})$	N_c	$\rho_{ions}/\text{nm}^{-3}$	R/nm	D_{AF}/s^{-1}	D_{des}/s^{-1}	$\Delta\mu/(\text{kJ/mol})$	Z	$K/(\text{m}^{-3}\text{s}^{-1})$	$\Delta G/(k_B T)$	$\log_{10}[J/(\text{m}^{-3}\text{s}^{-1})]$
8	89(4)	8.2074	0.6352	$0.4(3) \times 10^9$	2.7×10^9	4.55	0.0661	2.2×10^{35}	81(4)	0(3)
10	26(5)	9.7791	0.4215	$0.4(3) \times 10^9$	1.4×10^9	6.30	0.1440	5.6×10^{35}	33(6)	21(4)
12	12(4)	11.203	0.3257	$0.9(4) \times 10^9$	0.98×10^9	7.65	0.2336	2.4×10^{36}	18(6)	28(4)

Table 7.1. Seeding simulations data leading to the calculation of the nucleation rate. $\Delta\mu$, given per mol of ions in the table, has been taken from Refs. [53, 56, 55]. See main text for the meaning of each variable.

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In Table 7.1 the nucleation rates inferred from our Seeding simulations, and all variables leading to their calculation, are reported. The rate strongly depends on salt concentration and increases by almost 30 orders of magnitude when going from 8 to 12 mol kg⁻¹ concentration. In Sec. 7.5 we present the comparison of the nucleation rate data obtained by Seeding with those obtained by spontaneous crystallization (see next section) and those calculated with FFS in previous work [10].

7.4.2 Nucleation rate via brute force

At high concentrations, where ΔG is low, spontaneous nucleation of NaCl crystals can be seen in brute force molecular dynamics simulations. In Fig. 7.5 we show the number of particles in the largest NaCl cluster versus time for different trajectories started from a 15 mol kg⁻¹ solution. We see a cluster growing in all cases after some induction period that varies from run to run due to the stochastic nature of nucleation. The nucleation rate can be easily estimated from these simulations as:

$$J = \frac{1}{\langle t \rangle V}, \quad (7.8)$$

where $\langle t \rangle$ is the average time for observing spontaneous crystallization within the average simulation volume, V . To obtain these average properties we run 10 independent simulations starting from the same initial configuration and with different initial particle velocities (an example of such trajectories is shown in Fig. 7.5).

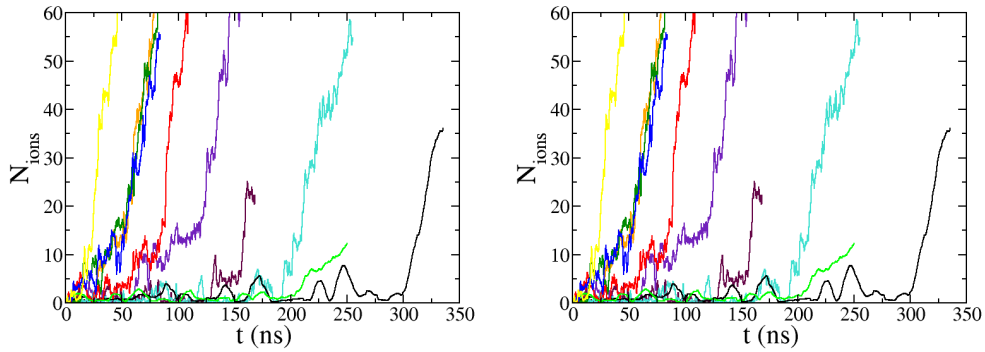


Figure 7.5. Number of particles in the largest NaCl crystal cluster along time for 15 mol kg⁻¹ systems. Each color represents one of the 10 independent simulations performed. Panels correspond to a) NVT and b) NpT ensembles at $T = 298.15$ K and $p = 1$ bar.

The crystallization time for a given trajectory is identified with that at which the number of particles in the cluster irreversibly shoots up (see Fig. 7.5). This criterion is subject to some arbitrariness which could introduce some error in the

average nucleation time. However, this error is small because the time that it takes to detect irreversible growth is much smaller than the nucleation time, as suggested by the abrupt increase of slope of the curves in Fig. 7.5 before and after irreversible growth.

In Table 7.2 we report the system sizes employed in our brute force simulations and the resulting nucleation rates, along with $\langle t \rangle$ and V . We present nucleation rates for concentrations ranging from 14 to 15 mol kg⁻¹. We also tried with 16 mol kg⁻¹ (with 14985 molecules of water and 4320 of NaCl) but we could not compute J since ions quickly aggregate and we observe the growth of a crystal nucleus in spinodal fashion without any induction period [65]. This is in agreement with Ref. [65] where a spinodal aggregation regime was found beyond 15 mol kg⁻¹. Therefore, the selected concentrations for the study of spontaneous crystallization are close to the onset of spinodal aggregation but still lie within the metastable equilibrium regime.

NpT						
m/(mol kg ⁻¹)	N_{NaCl}	N_{water}	$\langle t \rangle$ /ns	$\langle V \rangle$ /nm ³	p/bar	J /(m ⁻³ s ⁻¹)
15.00	4800	17760	47(24)	732.43	1	$3(1) \times 10^{31}$
14.71	37632	142080	16(8)	5822.18	1	$11(4) \times 10^{30}$
14.50	37120	142080	26(13)	5797.41	1	$7(2) \times 10^{30}$

NVT						
m/(mol kg ⁻¹)	N_{NaCl}	N_{water}	$\langle t \rangle$ /ns	V /nm ³	$\langle p \rangle$ /bar	J /(s ⁻¹ m ⁻³)
15.0	4800	17760	110(55)	731.19	93	$12(4) \times 10^{30}$
14.5	37120	142080	17(9)	5774.81	190	$10(3) \times 10^{30}$
14.0	35840	142080	31(16)	5715.07	189	$6(2) \times 10^{30}$

Table 7.2. Salt nucleation data leading to the calculation of J via brute force simulations in both NpT (top) and NVT (bottom) ensembles.

Coming back to the brute force simulations, in case that some runs do not show crystallization after a long time for a given concentration, we estimate J through the half-life time $t_{1/2}$, which in our case is the crystallization time for the 5th run to crystallize –recall that we launch ten in total– in increasing order of crystallization times. Then, we use the typical expression that relates the meanlife $\langle t \rangle$ and $t_{1/2}$ in a first order kinetic process to get an estimate of the former: $\langle t \rangle \approx t_{1/2} / \ln(2)$. The usefulness of this approach is that one does not need to wait for the ten trajectories to crystallize, which sometimes can take a very long time. For instance, a system at 15 mol kg⁻¹ (with 17760 molecules of water, 4800 of NaCl and volume 731.19 nm³) that was simulated over 10 independent runs in the NVT ensemble led to a mean nucleation time of $\langle t \rangle = 110.35$ ns (we show these trajectories in Fig. 7.5-a). Hence, we estimate the nucleation rate to be $J = 1.2 \times 10^{31} \text{ s}^{-1} \text{ m}^{-3}$. The 5th run to crystallize does it at 59.65 ns, which leads

$\langle t \rangle \approx t_{1/2}/\ln(2) \approx 86$ ns and to $J = 1.6 \times 10^{31} \text{ s}^{-1} \text{ m}^{-3}$, which is in good agreement with the direct measurement of runs that completed crystallization. Thus, this calculation gives a good approximation for the nucleation rate.

7.5 Discussion

We have used both NpT and NVT ensembles with no significant discrepancies, as it can be seen in Table 7.2 or in Fig. 7.5. Coming back to the previous example, we study the same 15 mol kg^{-1} system in the NpT ensemble. The average volume of the system in this case is 732.43 nm^3 and the mean nucleation time equals $\langle t \rangle = (47 \pm 7)$ ns. Then, the nucleation rate is $J = (29 \pm 4) \times 10^{30} \text{ s}^{-1} \text{ m}^{-3}$. In this case, as can be seen in Figure 7.5-b, the time evolution of the number of crystal-like ions suggests a critical cluster of around 9 ions. Due to the agreement of J obtained by either ensemble we can take the nucleation rate as the average: $J = 2 \times 10^{31} \text{ s}^{-1} \text{ m}^{-3}$. This data is in excellent agreement with the $J = 4 \times 10^{31} \text{ s}^{-1} \text{ m}^{-3}$ reported in Ref. [65] for the same model and at the same concentration. Such agreement gives us great confidence in our brute force simulations.

Another interesting information that can be inferred from the spontaneous nucleation runs is the size distribution of the solid-like clusters that spontaneously appear in the system. In Fig. 7.6 (a) we show the number of clusters containing a certain number of solid-like ions, $n_{N_{ions}}$, normalised by the total number of ions in the system, $2N_{NaCl}$. This distribution has been obtained by analysing the configurations generated in our 14.5 mol kg^{-1} runs before nucleation takes place. The solid clusters have been detected as described in Sec. 7.3. By taking $-\ln$ of $n_{N_{ions}}/(2N_{NaCl})$ we get an estimate of the nucleation barrier [64], as shown in Fig. 7.6 (b). The appearance probability of clusters larger than 9 ions is very small and the statistics are quite poor. To acknowledge such lack of statistics, data for $n_{N_{ions}} > 9$ are shown in dashed in Fig. 7.6 (b). The barrier height for the largest cluster that we can reliably sample ($N_{ions} = 9$) is $\sim 15 k_B T$, which is consistent with the $18.5 k_B T$ barrier height estimated by Seeding at 12 mol kg^{-1} (see table 7.1). The barrier seems to flatten beyond 9 ions (clusters with 10, 11 and 12 ions roughly have the same appearance probability), also consistent with 12-ions critical cluster Seeding estimate at 12 mol kg^{-1} . In any case, the dashed part of the curve shown in Fig. 7.6(b) should be just taken as a very rough estimate of the nucleation barrier given that in spontaneous crystallization one does not sample an equilibrium but rather a stationary state distribution of critical clusters. It is nonetheless worth mentioning that in Ref. [65] a nucleation barrier for the same model and a close concentration (15 vs 14.5 mol kg^{-1}) was rigorously computed with two different methods and the reported barrier (Fig. 2 in Ref. [65]) looks very similar to the one we give in Fig. 7.6 (b). Our simulations suggest that spontaneous nucleation is expected if clusters larger than ~ 10 ions –detected with the order parameter presented in Sec. 7.3– are observed in the simulations.

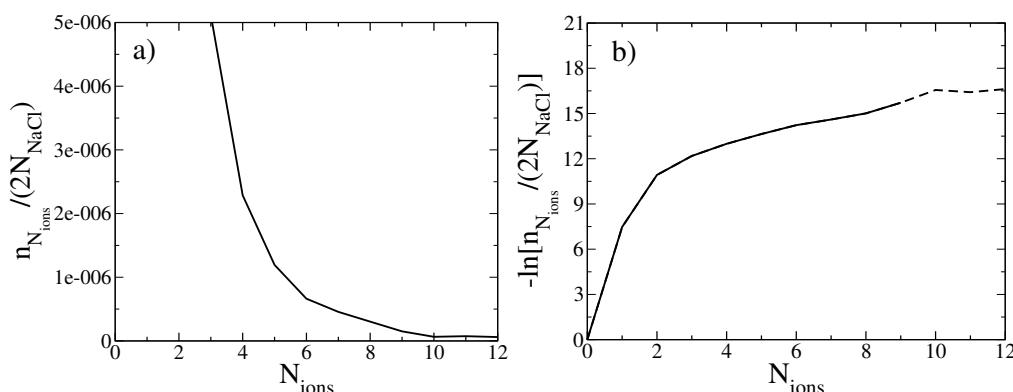


Figure 7.6. a) Number of clusters containing a given number of solid-like ions, $n_{N_{ions}}$, divided by the total number of ions for a 14.5 mol kg^{-1} solution; b) Free energy barrier estimated as $-\ln$ of such ratio. Data in b) beyond $N_{ions} > 9$ is shown in dashed because the probability of appearance of such clusters is very low and the statistics is poor.

Another property we can obtain from the simulated ionic solutions is the number of contact ion pairs, n^{CIP} :

$$n^{CIP} = \rho_{ions}/2 \int_0^{r_{min}} 4\pi r^2 g_{Na-Cl}(r) dr \quad (7.9)$$

where r_{min} is the first minimum of the $Na^+ - Cl^-$ radial distribution function, g_{Na-Cl} . We obtain 1.0 and 1.5 ion pairs for the 12 and 14.5 mol kg^{-1} solutions respectively. For NaCl, a number of CIP larger than 1.00 is a sign of warning for imminent spontaneous precipitation of the salt (as it often occurs in many force fields of NaCl which have a quite small value of the solubility as compared to the experimental one) [66, 67].

In Figure 7.7 we show the decimal logarithm of the nucleation rate as a function of the supersaturation, S , of the salty aqueous solution, defined as the ratio between the concentration of interest and the solubility. The black circles represent our estimation of the nucleation rate by Seeding calculations for concentrations of 8 mol kg^{-1} , 10 mol kg^{-1} and 12 mol kg^{-1} . The nucleation rate trend provided by Seeding follows quite nicely that of the FFS calculations by Jiang *et al.* [10]. However, Seeding always gives higher rates, being the discrepancy slightly larger for lower nucleation rates. It has been reported that FFS calculations are very demanding from a computational point of view and often yield underestimates of the nucleation rate [14, 68, 51]. Such problem becomes more accentuated for state points where the rate is low (low concentrations in our case) because tiny probabilities to reach the critical nucleus need to be sampled. This could explain the fact that the discrepancy between FFS and Seeding is larger for low concentrations in Fig. 7.7. Also for the case of hard spheres it seems that FFS gives lower rates than other techniques like Seeding or Umbrella Sampling the lower the driving force (i.e. lower pressures in this case) [41, 69]. In any case, the agreement between Seeding and FFS is quite reasonable. Moreover, Seeding is consistent with Brute

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Force estimates of the nucleation rate, which are represented with red circles (this work), orange diamonds (Ref. [10]), and a magenta star (Ref. [70]). We cannot extrapolate the Seeding results, which are based on CNT, to a higher supersaturation (beyond 15 m [65]) where crystallization is expected to take place in a 2-step spinodal fashion as opposed to a classical 1-step mechanism [65, 71, 65]. In general, the Seeding approach employed in this work is only valid in principle for classical 1-step nucleation pathways that can be described within the CNT framework. There are several instances where solute precipitation is thought to be a multiple-step process [6, 72, 73, 74] where the approach presented in this paper would not be suitable.

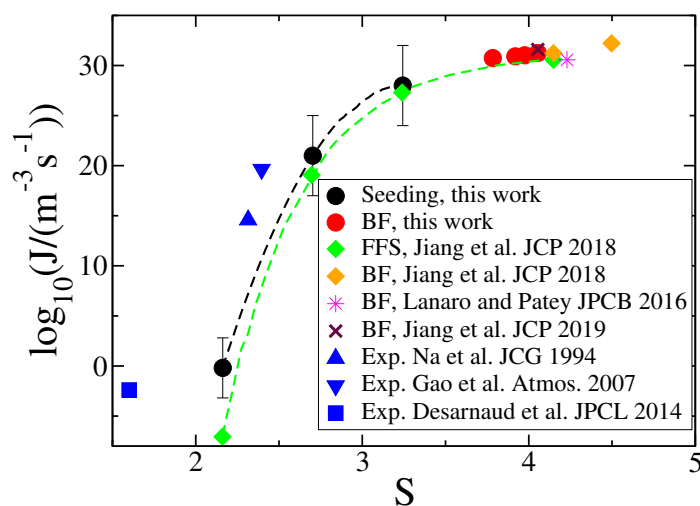


Figure 7.7. Decimal logarithm of the nucleation rate of NaCl in aqueous solution as a function of supersaturation, S , defined as the ratio between the concentration of interest and the solubility concentration (both in molality units). Black circles correspond to nucleation rates estimated from Seeding and red circles to rates estimated from Brute Force (BF), both obtained in this work. The black dashed curve is a guide for the eyes for our seeding data. Diamonds are nucleation rates reported by Jiang *et al.* [10], green corresponding to forward flux sampling method and orange to BF. Magenta star is the BF nucleation rate estimated from the induction times reported by Lanaro and Patey [70]. Maroon cross is the BF nucleation rate estimated with MFPT reported by Jiang *et al.* [65]. Filled blue symbols are values of the nucleation rate estimated in Ref. [22] from the experiments by Na *et al.* [76] (up triangle), Gao *et al.* [75] (down triangle) and Desarnaud *et al.* [77] (square).

In this paper we revisit a study performed a few years ago where it was concluded that Seeding does not provide accurate values of the rate because the results strongly depend (by tens of orders of magnitude) on the choice of the order parameter used to detect the cluster size [22]. Although we subscribe to such statement, here we show that when the mislabelling criterion is employed to tune the order parameter, Seeding yields reasonable results in agreement with independent techniques that do not have such dependence on the order parameter. With

such mislabelling criterion, Seeding has also been consistent with independent methods for a wide variety of systems ranging from hard spheres to water [41]. Therefore, this work provides further support to the use of the mislabelling criterion as a means to identify the cluster size relevant for CNT in crystal nucleation studies.

Finally we compare the model predictions for the nucleation rate with experimental data. Bear in mind that the comparison between model and experiments is not straightforward since the model solubility, 3.7 mol kg^{-1} , is different from the experimental one, 6.1 mol kg^{-1} . To enable a sensible comparison, model results and experimental data are plotted against the supersaturation in Fig 7.7. It is also worth noting that experimental data are not direct measurements of the nucleation rate, but estimates made on the supplementary material of Ref. [22] based on efflorescence [75], electrodynamic balance drop levitation [76], and capillary crystallization [77] experiments. For a given supersaturation, the experimental data lie above the model. This means that the model requires higher supersaturations to achieve the same crystallization rate as in experiments. It would be highly desirable to have a model that reproduces both the experimental solubility of NaCl and its crystal nucleation rate, but this is not the case of the JC/SPC/E model used here, that gives reasonable predictions but with a wide margin for improvement. Hopefully, the big effort currently being devoted to the development of force fields to simulate NaCl-H₂O mixtures will give rise to such a good model [78, 79, 80, 66].

7.6 Conclusions

In this work we have obtained nucleation rates of NaCl in supersaturated aqueous solutions using the JC/SPC/E model. To do so, we have applied both the Seeding technique and brute force simulations. Seeding results extrapolate very well toward brute force results. Moreover, the agreement of seeding and previous works using rigorous techniques like FFS is quite reasonable. Thus, this work suggests that as long as a good order parameter is implemented in the Seeding scheme, this can be a very powerful approach to study nucleation even in complex media as ionic solutions.

The determination of the critical cluster size is indeed the most delicate issue in the Seeding method. Different criteria may lead to substantial differences in the rate estimates, as concluded in Ref. [22]. Motivated by Ref. [22], and by the fact that the Mislabelling criterion has proven successful in the past for hard spheres [41], Lennard Jones [41], water [81] and, more recently, oppositely charged colloids [51], we decided to use the Mislabelling criterion for the case of NaCl precipitation from a brine solution. We do not have a proof that the Mislabelling criterion must necessarily work. The fact that the criterion works for a Seeding study of NaCl crystallization from the brine is an empirical finding of this paper. In principle the Mislabelling criterion seems a very reasonable approach

because, by construction, it equally favours or penalises both bulk phases involved in the phase transition. However, just being "reasonable" is not a guarantee of success and one has to test it for every specific case, which is precisely what we do in this work for NaCl nucleation from solution. The list of systems for which the Mislabelling criterion combined with Seeding gives satisfactory estimates of the nucleation rate is quite wide now, making a strong case for the use of this approximate although powerful approach to study nucleation.

7.7 Acknowledgments

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The water cavitation line as predicted by the TIP4P/2005 model

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8.1 Abstract

The formation of vapour bubbles in a metastable liquid, cavitation, is an activated process due the free energy cost of having both phases at contact. Such an energetic penalty enables the existence of the liquid beyond its thermodynamic borders. Establishing the stability limits of a liquid as ubiquitous as water has important practical implications and has thereby attracted a lot of attention. Different experimental strategies and theoretical analyses have been employed to measure and predict the cavitation line, or the pressure-temperature kinetic stability border of liquid water. Understanding the location of the cavitation line requires knowing the cavitation rate dependence with pressure and temperature. Such dependency is difficult to obtain in experiments, and we use molecular simulations with the TIP4P/2005 model to fill this gap. By deeply overstretching liquid water below the saturation pressure we are able to observe and quantify spontaneous cavitation. To deal with a lower overstretching regime we resort to the Seeding technique, which consists in analysing simulations of a liquid containing a vapour bubble under the theoretical framework of Classical Nucleation Theory. Combining spontaneous cavitation with Seeding we get a wide overview of the cavitation rate along pressure. We study two different temperatures (450 and 550 K) and complement our perspective with the results previously obtained at 296.4 K [Menzl et al. PNAS 2016] to establish a broad simulation-experiment comparison. We find a good agreement between simulations and both isobaric heating and isochoric cooling

experiments using quartz inclusions. We are however unable to reconcile simulations with other experimental techniques. Our results predict a decrease of the solid-liquid interfacial free energy as the liquid becomes increasingly overstretched with a temperature independent Tolman length of 0.1 nm. Therefore, the capillarity approximation underestimates the nucleation rate. Nonetheless, it provides a fair indication of the location of the cavitation line given the steep rate versus pressure dependence. Overall, our work provides a comprehensive view of the water cavitation phenomenon and sets an efficient strategy to investigate it with molecular simulations.

8.2 Introduction

Many microwave ovens display a sticker with a symbol recommending to place a spoon in the mug where water is heated. The spoon acts as a surface to aid the emergence of vapour bubbles. When bubbles are formed, a liquid-vapour equilibrium is established and heat transferred by microwaves is employed in increasing the number of molecules in the vapour phase rather than in a further temperature raise. In the absence of a spoon, however, bubbles may not form and the liquid may get superheated beyond the boiling temperature. In such case, water can boil explosively when handled by the user. Superheating is not the only manner to have metastable liquid water with respect to the vapour. Metastability can also be achieved by overstretching the liquid below the vapour saturation pressure. This route enables probing negative pressures, which is of great interest for the study of the thermodynamic behaviour of liquid water and the understanding of its anomalies [1, 2, 3, 4]. The emergence of vapour cavities in the metastable liquid (cavitation) sets the limit for the superheating or the overstretching that the liquid can sustain. Cavitation plays an important role in many industrial, technological and geological processes [5, 6, 7, 8, 9, 10, 11], which makes the understanding of the physics that governs it of paramount importance.

This interest has prompted numerous experimental studies of water cavitation where vapour bubbles arise upon isobaric heating [12], application of acoustic waves [13, 14] or isochoric cooling [1, 15, 16, 17, 18]. In these experiments, the metastability limit of the liquid with respect to the vapour is determined. The boundary between the metastable liquid and the vapour is a cavitation line in the pressure-temperature plane below which bubbles readily nucleate [1, 19, 20]. This cavitation line is analogous to the so-called homogeneous ice nucleation line [21], that sets the temperature boundary (along pressure) for the metastability of the liquid with respect to ice. In both metastability situations (liquid vs vapour and liquid vs solid) it is the unfavourable interfacial free energy between the emerging phase (vapour or ice) and the surrounding liquid that enables the survival of the latter beyond its thermodynamic stability limits [22, 23].

Experimental investigations on cavitation have been complemented by theoretical work in the framework of Classical Nucleation Theory (CNT)[24, 25, 2]

or, more recently, Density Functional Theory [20], with the aim of predicting and understanding the location of the cavitation line. The agreement between theoretical predictions and experiments is quite satisfactory [1, 20, 19] provided that the interfacial free energy between the liquid and the vapour is allowed to decrease when moving away from coexistence [20, 2].

An important drawback of both theory and experiments is that they do not have access to detailed information at the molecular scale. For instance, the critical bubble (that having a 50 per cent chance of either growing or redissolving) cannot be visualised experimentally due to its small size and short lifetime. Computer simulations can bridge this gap and they have been extensively used to study cavitation in model systems like the Lennard-Jones fluid [26, 27, 28, 29, 30, 31, 32, 33]. Simulation work for water cavitation is more scarce, though, due to the technical difficulty of studying a rare event like cavitation –that requires the use of special simulation methods– in a costly system from a computational point of view due to the presence of electrostatic interactions. Ref. [3] pioneers the simulation work on water cavitation. With the use of biased simulations that promoted the appearance of bubbles in the overstretched liquid the authors of Ref. [3] were able to calculate the nucleation rate versus the liquid pressure for temperature $T = 296.4$ K. The nucleation rate –the number of critical bubbles that appear per unit of time and volume– is the central parameter in nucleation. By knowing the nucleation rate, one can estimate the pressure at which cavitation is going to take place in a certain experimental set up, which means that one can predict the location of the cavitation line. In fact, the authors of Ref. [3] report a cavitation pressure of -126 MPa at the studied temperature and for the selected water model (TIP4P/2005 [34]), which is in line with the measurements obtained in isochoric cooling in quartz inclusions [1, 15], although at odds with acoustic cavitation experiments [35, 36, 14, 37, 36].

In this paper, we revisit cavitation of overstretched water with simulations using the TIP4P/2005 water model [34]. We focus on two different temperatures as compared to Ref. [3], namely 450 K and 550 K, enabling a more direct comparison with the regime where most experimental points of the homogeneous cavitation line are available. Moreover, we use an efficient computational approach based on directly simulating the liquid with a vapour bubble already formed at the beginning of the simulations [38, 39, 40]. This strategy, called Seeding [41, 42, 43, 44, 45, 29], combines average properties obtained in the simulations of the vapour bubbles with the theoretical formalism of CNT [46, 47, 48]. We complement Seeding with unbiased “brute force” molecular simulations in a high overstretching regime where bubbles appear spontaneously. Although such regime is not attainable in experiments, we use brute force results to validate Seeding simulations, that do overlap with experimentally relevant conditions.

Our simulation results for the location of the homogeneous cavitation line compare satisfactorily with theoretical predictions [25, 20] and experimental measurements [1, 15]. Simulated bubbles have an interfacial thickness of about 1 nm for 450 K and 2 nm for 550 K. The equi-density [28] definition of the bubble

radius gives a better consistency between Seeding and Brute Force simulations than the Gibbs equi-molar surface. A decrease of the interfacial free energy as vapour bubbles become smaller (or as pressure decreases) is inferred from our simulations. We also find that the vapour bubble pressure obtained by equating its chemical potential to that of the surrounding liquid is consistent with that given by the density in the interior of the bubble. This result, although expected, is not verified in liquid-to-solid phase transitions [49, 50, 51]. Overall, our work shows that water cavitation can be studied from a molecular perspective giving experimentally relevant information in a rather efficient manner.

8.3 Simulation details

We use the TIP4P/2005 force field for water, which is a rigid model consisting of three fixed point charges and one Lennard-Jones (LJ) centre [34].

Molecular dynamics simulations are performed with the GROMACS package 2018 (single precision) [52]. When simulating in the NpT ensemble, we use the Parrinello-Rahman barostat [53], with a relaxation time of 2 ps and a compressibility of 10^{-5} bar^{-1} . To control the temperature we use the Nosé–Hoover thermostat [54] with a relaxation time of 2 ps. For the Verlet integration of the equations of motion, we use a time step of 2 fs. To deal with electrostatic interactions we use particle mesh Ewald summations [55]. The cut-off radius for the neighbour list, the dispersive Lennard Jones interactions and the real part of the electrostatic interactions is 13 Å. Ewald summations have been previously used to deal with heterogeneous systems [56], including water bubbles [3, 57]. We have checked for specific cases of bubble simulations that the energy barely changes by increasing the Ewald cutoff to 20 Å. Moreover, we find that even using a plain 20 Å cutoff for the electrostatic interactions does not almost change the average energy. These arguments give us confidence in the use of Ewald summations with the selected 13 Å real part cutoff. No tail corrections are added to the Lennard Jones potential due to the presence of two phases with strongly different densities in our simulations. We use a switch radius of 12 Å, meaning that the LJ potential is not modified up to this radius, after which it is gradually switched off to reach zero at the cut-off radius. The LINCS algorithm is used to fix the geometry of the water molecules, with an order of 6 and 4 iterations [58, 59].

8.4 Results

Most results discussed below correspond to a temperature of 450 K. Only at the end, in Section 8.4.2, we add results corresponding to 550 K in order to establish a broader comparison with experiments.

8.4.1 Coexistence properties

The liquid-vapour equilibrium for this model has been characterised in Ref. [60]. We recalculate here the coexistence pressure at $T = 450\text{ K}$ to both test our simulation set up and to account for the use of a slightly different cutoff radius. We first equilibrate a liquid of 4096 water molecules in a cubic box in the NpT ensemble. After, we introduce some empty space next to the liquid, finishing with a box of $3.91724 \times 3.91724 \times 27.14\text{ nm}$. We run this system (in the NVT ensemble) until equilibrium has been reached and obtain the pressure components of the system. The pressure component normal to the vapour-liquid interface is the vapour (or coexistence) pressure and it does not depend on the system size; in our case $p_z = 4.49\text{ bar}$, in very good agreement with the values reported in Ref. [60] (4.46 bar) and Ref. [61] (4.5 bar). The tangential components of the pressure depend on the system size and in our case are $p_x = -24.38\text{ bar}$ and $p_y = -24.48\text{ bar}$. The interfacial free energy at coexistence, γ_c , is obtained using the mechanical route [62]:

$$\gamma_c = \frac{L_z \left[p_z - \frac{p_x + p_y}{2} \right]}{2} \quad (8.1)$$

We obtain $\gamma = (40 \pm 1)\text{ mJ m}^{-2}$, which is similar to the value calculated in Ref. [61], $\gamma = 38.8\text{ mJ m}^{-2}$.

8.4.2 Cavitation rate

Cavitation rate by brute force molecular dynamics simulations

By lowering the pressure of the liquid below the coexistence value one should observe the nucleation of vapour cavities (cavitation). Owing to the liquid-vapour interfacial free energy, this process is activated and can take a long time. At very low pressures, however, the thermodynamic drive for the emergence of the vapour phase is high and the cavitation process is relatively quick. In fact, it is possible to observe it in brute force molecular dynamics simulations of the bulk liquid for negative pressures below -650 bar . This is shown in Fig. 8.1, where we plot the volume of the simulation box versus time for 10 different trajectories starting from a bulk liquid consisting of 20000 water molecules under periodic boundary conditions at 450 K and -700 bar . In all runs, the system abruptly increases its volume after some induction period (which varies stochastically from one trajectory to another) due to the sudden appearance and growth of a vapour bubble. The stochastic character of cavitation is a consequence of its activated nature. The fact that there is a long induction period indicates that a single bubble is formed in the system (an unlikely event does not happen twice or more at the same time). This enables us to estimate the bubble nucleation rate as:

$$J = \frac{1}{\langle t \rangle \langle V \rangle}, \quad (8.2)$$

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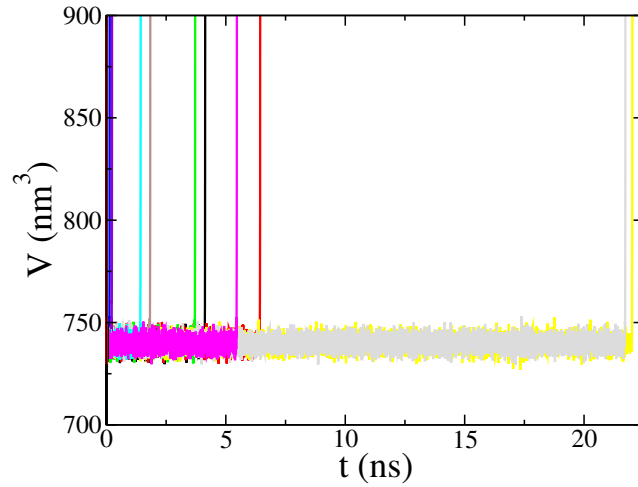


Figure 8.1. Volume of the simulation box versus time starting from 10 liquid configurations containing 20000 molecules. The thermodynamic state point is 450 K and -700 bar.

using 1 in the numerator because one only bubble forms in each run. $\langle t \rangle$ is the average time that it takes to observe the nucleation of a bubble, which is obtained as the arithmetic average between the times at which the volume sharply shoots up in our 10 trajectories. $\langle V \rangle$ is the average volume of the liquid where bubble nucleation takes place. In Table 8.1 we report the nucleation rates for different pressures alongside the variables required to compute them. Obviously, the lower the pressure the higher the cavitation rate. With our brute force calculations we span three orders of magnitude of the nucleation rate: from $10^{33} \text{ m}^{-3} \text{ s}^{-1}$ at -750 bar to $10^{30} \text{ m}^{-3} \text{ s}^{-1}$ at -650 bar. Probing lower nucleation rates with brute force calculation is too demanding computationally. It is important, however, to get estimates of lower nucleation rates given that in experiments one has access to rates of the order of [20] $10^{15} \text{ m}^{-3} \text{ s}^{-1}$. To do that, we resort to the Seeding technique, that is described in the following section.

p (bar)	$\langle t \rangle$ /ns	$\langle V \rangle$ /nm ³	J /(s ⁻¹ m ⁻³)
-750	0.5(2)	747.8(1)	3×10^{33}
-725	1.1(2)	743.73(6)	$12(2) \times 10^{32}$
-700	7(3)	739.81(3)	$20(8) \times 10^{31}$
-675	40(10)	736.15(1)	$31(8) \times 10^{30}$
-650	300(100)	732.798(7)	$4(2) \times 10^{31}$

Table 8.1. Data leading to the calculation of J via brute force molecular dynamics simulations using a system of 20000 TIP4P/2005 water molecules at 450 K.

Cavitation rate via *NVT* Seeding

We shall compute the nucleation rate for higher pressures (lower rates) using Seeding [44, 43, 41, 42, 45]. In this method, instead of waiting for a bubble to spontaneously appear, the simulation is started from a configuration of a liquid containing a bubble. When equilibrated in the *NVT* ensemble, the bubble turns out to be the critical vapour nucleus at the simulation temperature and at the pressure acquired by the surrounding liquid [29]. With such pressure, and the bubble radius one can obtain an estimate of the nucleation rate using CNT [29].

To prepare the initial configuration we first equilibrate liquid water in the *NpT* ensemble at 450 K and a selected pressure below saturation. Next, we remove the molecules inside a sphere in the centre of the box. This system is then simulated in the *NVT* ensemble and allowed to equilibrate during 1 ns. We repeat this process with different pressures, box sizes and cavity radii looking for trajectories having a stable vapour bubble (stabilising spherical nuclei in the *NVT* ensemble is not always viable and depends on a subtle balance between the size of the box and that of the nucleus [29, 50]). In Table 8.2 we summarise the system sizes employed in our Seeding simulations alongside the radii of the stabilised bubbles averaged over 19 ns. We report two different radii for each bubble. One is R_G , the radius corresponding to the equi-molar Gibbs dividing surface, which is computed as follows:

$$R_G = \left(\frac{3(N - L^3 \rho_l)}{4\pi(\rho_v - \rho_l)} \right)^{1/3} \quad (8.3)$$

where N is the total number of molecules, L is the length of the simulation box edge (since we work with a cubic system the volume of the box is L^3) and ρ_l and ρ_v are the densities of the liquid and the vapour phases respectively. The former is obtained via the average virial pressure, p_l , and the bulk liquid equation of state (see Table 8.2). The latter, by looking for the vapour that has the same chemical potential as the surrounding liquid [63, 64]: $\mu_l(T, p_l) = \mu_v(T, p_v)$. We search where this condition is satisfied by performing isothermal thermodynamic integration of both the bulk vapour and the bulk liquid molar volumes from the coexistence pressure, p_{coex} , as described in Ref. [28]. In Fig. 8.2 we show $\mu(p) - \mu(p_{coex})$ at 450 K for the liquid (black curve) and the vapour (red curve). The dotted vertical line at $p = -295.4$ bar corresponds to p_l for a bubble of 2.5 nm. The chemical potential of such liquid can be obtained from the intersection between the dotted line and the black curve. Then, we read from the intersection between the horizontal dashed line and the red curve, the pressure of the vapour that has the same chemical potential of the liquid, p_v . Δp , a key parameter in the CNT nucleation formalism, is the difference between p_v and p_l . The vapour pressures, p_v , and the corresponding densities, ρ_v , thus obtained for all simulated bubbles are reported in Table 8.2.

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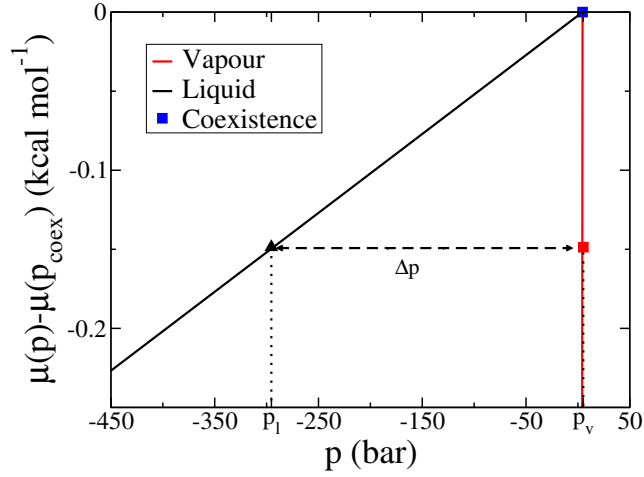


Figure 8.2. Chemical potential difference with respect to the coexistence pressure at 450 K for the bulk liquid (black) and the bulk vapour (red) phases. Dashed and dotted horizontal and vertical lines guide the search for the condition of equal chemical potential in a bubble of radius 2.5 nm (see main text for more details).

Alternatively, we compute the bubble radius by means of an average radial density profile starting from the bubble centre, as that shown in Fig. 8.4. Such a density profile is fitted to the following sigmoid function (dashed orange curve in Fig. 8.4):

$$\rho(r) = \frac{\rho_{v,dp} + \rho_{l,dp}}{2} + \left(\frac{\rho_{l,dp} - \rho_{v,dp}}{2} \right) \cdot \tanh[(r - R_{ed})/\alpha] \quad (8.4)$$

where $\rho_{v,dp}$ and $\rho_{l,dp}$ are the densities of the vapour and the liquid phases obtained with the density profile (dp) fit, α is a parameter related to the width of the interfacial region, and R_{ed} is the critical bubble radius estimated as the distance at which the density is the average between both phases (“equi-density” criterion) [28]. The equi-density radius, R_{ed} , reported in Table 8.2, is close to, but systematically lower than R_G .

Both approaches to obtain the radius (Eqs. 8.3 and 8.4) assume a spherical bubble shape. In order to visually inspect the shape we provide in Fig. 8.3 a series of slab cuts through the bubble centre at different times along a Seeding simulation containing a 2.5 nm bubble. The sequence of snapshots clearly shows that the bubble shape fluctuates around a sphere, which justifies our approach to obtain the bubble radius assuming an average spherical shape.

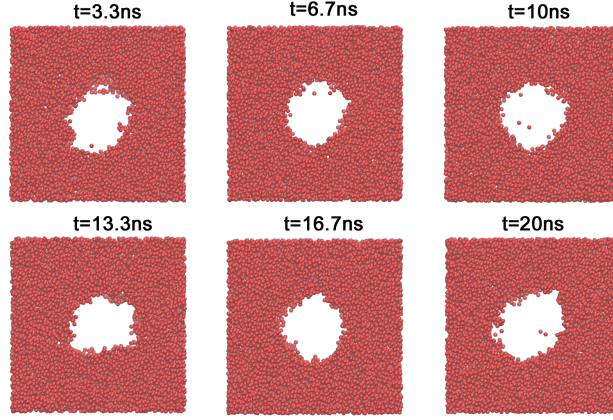


Figure 8.3. Slab cuts of 20 Å thickness through the bubble centre in a Seeding simulation at 450 K containing a ~ 2.5 nm radius sphere.

The fit parameter in Eq. (8.4) $\rho_{l,dp}$ is fully consistent with the density obtained by means of the overall virial pressure of the system and the bulk liquid equation of state. However, the vapour density provided by the fit given by Eq. (8.4), $\rho_{v,dp}$, is not accurate given the small size of the bubbles (the sigmoid does not reach a true plateau in the interior of the bubble). Nevertheless, by estimating the vapour density as an average of the density profile in a region in the interior of the bubble, one does obtain consistent values with the vapour density resulting by imposing equal chemical potential between the bubble and the surrounding liquid. This consistency, although expected, should not be given for granted. For instance, for hard sphere crystallisation, the density (and the mechanical pressure) of the crystal nucleus is lower than that obtained by imposing chemical potential homogeneity (in fact, the nucleus mechanical pressure is even lower than that of the surrounding liquid) [49, 50, 51].

Knowing the bubble radius and Δp we can use CNT to estimate the nucleation rate, J :

$$J = A \exp\left(-\frac{\Delta G_c}{k_B T}\right) \quad (8.5)$$

where k_B is the Boltzmann constant, A is a kinetic pre-factor, and ΔG_c is the Gibbs free energy associated with the formation of the critical bubble, which is given by:

$$\Delta G_c = \frac{2\pi \times \Delta p \times R_c^3}{3}. \quad (8.6)$$

where R_c is the critical bubble radius that we identify either with R_G or with R_{ed} . The kinetic pre-factor is computed following Blander and Katz [24]:

$$A = \sqrt{\frac{\Delta p \times R_c}{\pi m}} \rho_l \quad (8.7)$$

where m is the mass of the molecule (18.02 u for water). This theoretical expression gives consistent results with other routes to estimate the kinetic pre-factor

[65]. One can also obtain from the bubble properties an estimate of the interfacial free energy via the Laplace equation:

$$\gamma = \frac{\Delta p \times R_c}{2} \quad (8.8)$$

In Table 8.2 we provide the nucleation rates for all simulated bubbles alongside all parameters required for their computation. The kinetic pre-factor A can be obtained with the data reported in the table using Eq. (8.7) and is of the order of $10^{40} \text{ m}^{-3} \text{ s}^{-1}$ for all pressures and both choices of radius definition. The rates corresponding to R_G and R_{ed} are shown as filled black and red circles respectively in Fig. 8.5. Our data are consistent with those of Ref. [20], indicated with crosses in the figure, which were obtained with Density Functional Theory for two different temperatures, namely 423 and 523 K.

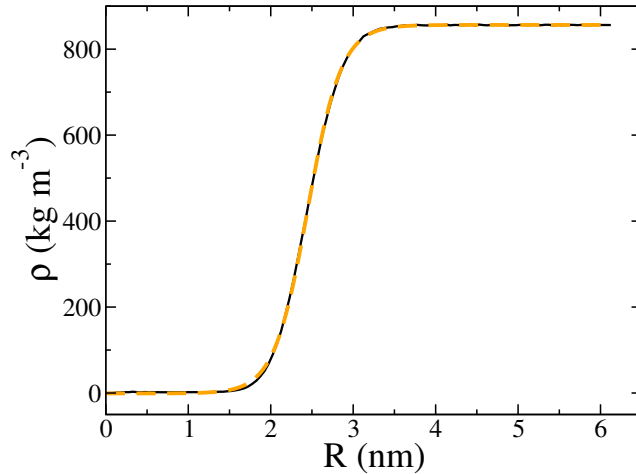


Figure 8.4. Radial density profile starting from the bubble centre averaged over 19 ns in the NVT ensemble (black line). The profile corresponds to a bubble surrounded by a liquid of pressure -295.4 bar. Dashed orange line is a fit to the simulation data given by Eq. (8.4).

Surface free energy and the capillarity approximation

The surface free energy, γ , between the bubbles equilibrated in the NVT Seeding simulations and the surrounding liquid can be estimated from Eq. (8.8). We report them in Table 8.2 for all bubbles and plot them in Fig. 8.6 as a function of the liquid pressure. Again, black and red symbols correspond to the Gibbs and the equi-density definitions of the critical bubble radius respectively. Both sets of data tend to the flat interface value (blue square) obtained from our liquid-vapour direct coexistence simulations via Eq. (8.1). This is a good consistency test passed by the Seeding approach. Given that γ is proportional to the bubble radius (see Eq. (8.8)) and that $R_{ed} < R_G$, γ coming from the equi-density radius definition

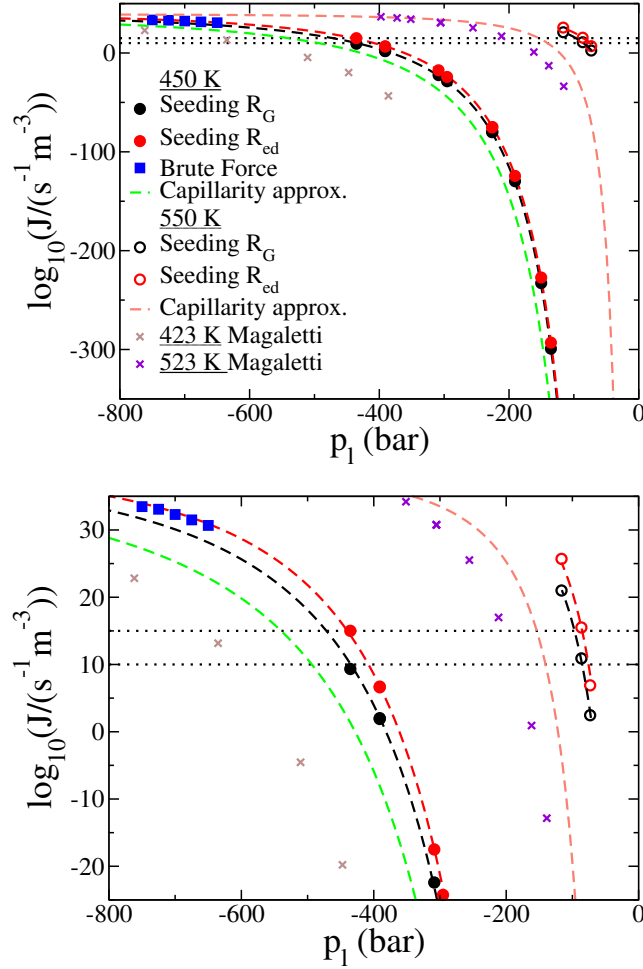


Figure 8.5. a) Decimal logarithm of the cavitation rate as a function of the liquid pressure. Blue squares are obtained by Brute Force simulations at 450 K. Circles are obtained with *NVT* Seeding (black circles using the Gibbs definition for the critical bubble radius (Eq. (8.3)) and red ones the equi-density criterion (Eq. (8.4))). Filled circles correspond to $T = 450$ K and empty ones to 550 K. The black and red dashed lines are fits to the *NVT* Seeding data using the CNT expressions given in the main text and the $\gamma(p)$ dependence shown in Fig. 8.6. The green (pink) dashed line represents the capillarity approximation for 450 K (550 K). The horizontal dotted lines indicate the expected rate range for cavitation in isobaric superheating [12] and quartz inclusions isochoric cooling experiments [1, 15]. Crosses correspond to Density Functional Theory for 423 K (brown) and 523 K (purple) [20]. b) Enlargement of the high nucleation rate regime.

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is systematically lower. As one approaches coexistence (higher pressures/larger bubbles) both sets of data get closer to each other because the difference between both radii becomes a small fraction of the overall radius. The decrease of γ with pressure for the equi-density radius definition is about 1 nNm^{-1} per 100 bar pressure drop, whereas it is approximately half that for the Gibbs radius. In either case, γ goes down by decreasing the pressure away from coexistence. This is consistent with the results obtained in Ref. [3] at another temperature (296.4 K).

The lowering of γ by moving away from coexistence is a common feature with other systems like the Lennard-Jones fluid in the cavitation/condensation transition [28, 29, 30, 33] or ice nucleation in water [44, 66]. In our case, both the curvature of the interface and the pressure of the surrounding fluid change by moving away from coexistence. Both factors simultaneously contribute to the variation of γ and their effects cannot be decoupled. Nevertheless, it seems intuitive that by lowering the pressure (or the density) of the liquid the similarity between the vapour and the liquid increases, which is goes in line with a γ decrease.

The decrease of γ with pressure looks rather linear (see Fig. 8.6 (a)). By fitting $\gamma(p)$ to a straight line (dashed in Fig. 8.6) and using Eqs. (8.5) to (8.8) we can fit the rate-pressure dependence [29] and obtain the dashed curves in Fig. 8.5 that we comment in more detail in the following section.

The variation of γ with curvature is often described by the following expression proposed by Tolman [64]:

$$\gamma = \gamma_c \left(1 - \frac{2\delta}{R_c} \right) \quad (8.9)$$

where δ is the Tolman length, that can be obtained from the slope of a γ vs $1/R_c$ representation such as that shown in Fig. 8.6c) (filled data correspond to 450 K). We use $R_c = R_{ed}$ to do such representation given that, as it will be shown later on, it turns out that R_{ed} better predicts the nucleation rate in the spontaneous cavitation regime. A positive δ is expected given that γ diminishes as curvature increases. The resulting δ is 0.1 nm. Later on, in Section 8.4.2, we extend our study to temperature 550 K in order to compare our simulations with experiments. Here, we anticipate the results for this temperature regarding the Tolman length. From the representation in Fig. 8.6c) (empty symbols) we get the same δ as for 450 K, 0.1 nm, suggesting that δ is temperature independent. A very recent simulation estimate of δ at T=296.4 K ($0.091 \pm 0.008 \text{ nm}$) using the same model as in this work confirms the non-dependence of the Tolman length with temperature.

Taking into account the decrease of γ when lowering the liquid pressure is crucial to get accurate estimates of the nucleation rate. To illustrate this we compute the rate that would be obtained by considering γ constant and equal to its value at coexistence (capillarity approximation). To obtain such rate we express Eq. (8.7) and Eq. (8.6) as a function of γ via Eq. (8.8). Thus, one gets:

$$\Delta G_c = \frac{16\pi\gamma^3}{3\Delta p^2} \quad (8.10)$$

and:

$$A = \rho_l \sqrt{\frac{2\gamma}{\pi m}}. \quad (8.11)$$

Inserting Eq. (8.11) and Eq. (8.10) into Eq. (8.5) and using the coexistence γ for every pressure gives rise to the green dashed curve in Fig. 8.5 that lies at lower rates as compared to Seeding or Brute Force data. The capillarity approximation actually underestimates J by 6 orders of magnitude when compared to Brute Force. The conclusion is that a theoretical or a simulation treatment (Seeding and Brute Force in the present case) that takes into consideration the variation of γ with pressure/curvature is indeed needed to obtain accurate cavitation rates in overstretched water, not being enough the use of the capillarity approximation. That the capillarity approximation fails to provide accurate nucleation rates for water cavitation was also concluded in previous simulation and theoretical studies [3, 20, 2].

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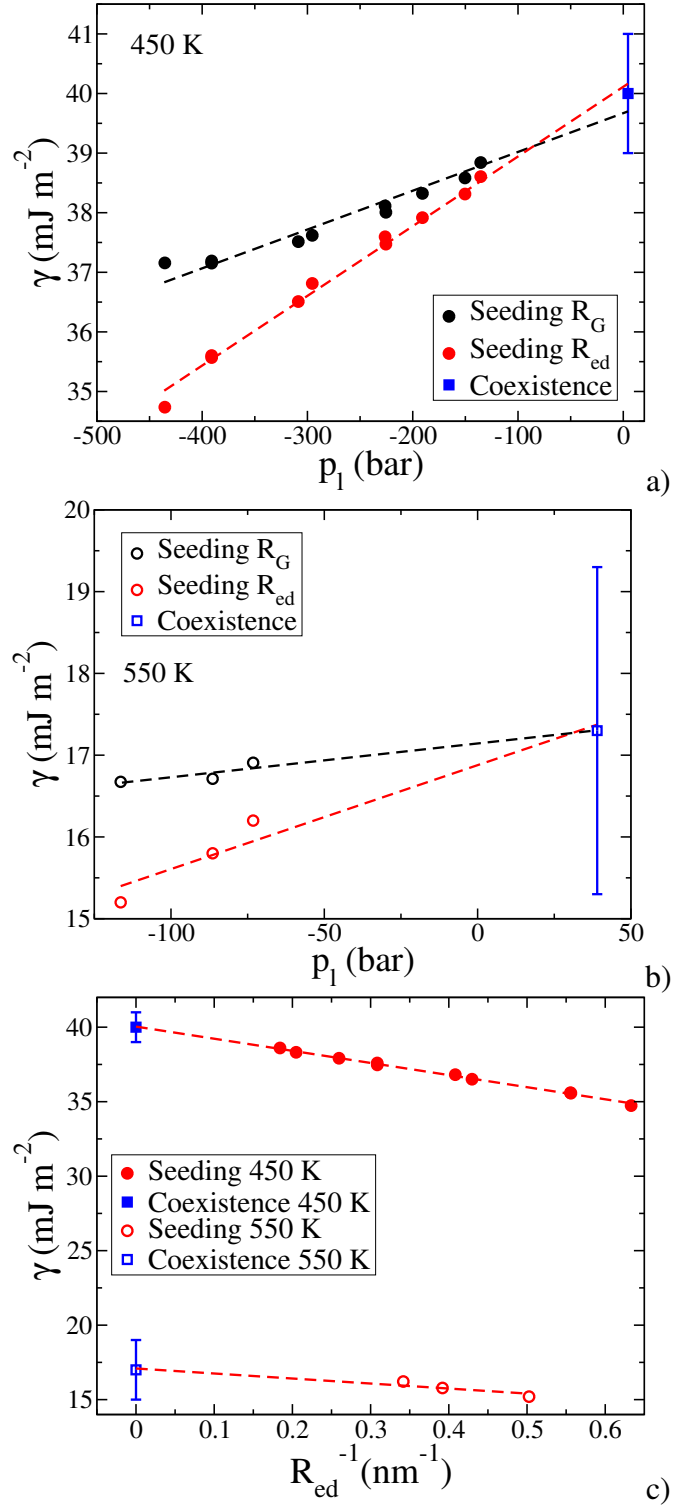


Figure 8.6. a) and b) Interfacial free energy as a function of the liquid pressure. Black and red symbols correspond to estimates of γ from the NVT Seeding simulations using Eq. (8.3) and Eq. (8.4) to obtain the bubble radius respectively. The blue square corresponds to the coexistence value obtained with simulations of a flat vapour-liquid interface via Eq. (8.1). a) and b) correspond to 450 and 550 K respectively. c) Interfacial free energy versus the inverse equi-density radius for both temperatures as indicated in the legend.

T (K)	N	L (nm)	p_l (bar)	Δp (bar)	ρ_l (kg/m ³)	ρ_v (kg/m ³)	R_{ed} (nm)	R_G (nm)	$\log_{10}(J_{ed}/(\text{s}^{-1} \text{m}^{-3}))$	$\log_{10}(J_G/(\text{s}^{-1} \text{m}^{-3}))$
450	58817	13.9305	-135.4	142.2	869.8	3.79	5.43	5.46	-293	-299
	64085	13.9305	-150.4	156.9	868.6	3.65	4.88	4.92	-227	-233
	47110	12.3315	-190.8	196.8	865.2	3.34	3.85	3.89	-124	-130
	49774	12.3315	-225.5	231.2	862.2	3.13	3.24	3.29	-75	-80
	49774	12.3315	-226.2	231.9	862.2	3.12	3.24	3.29	-75	-80
	51785	12.3315	-295.4	300.6	856.0	2.79	2.45	2.50	-24	-29
	17985	8.8216	-308.7	313.7	854.8	2.73	2.33	2.39	-17	-22
	18548	8.8056	-391.0	395.6	847.0	2.44	1.80	1.88	7	2
	18524	8.8023	-391.0	395.6	847.0	2.44	1.80	1.88	7	2
	8950	6.9651	-435.5	439.8	842.6	2.31	1.58	1.69	15	9
550	50691	13.1049	-73.2	110.9	710.2	20.92	2.93	3.05	7	2
	17064	9.2936	-86.4	123.7	706.6	20.56	2.55	2.70	16	11
	17737	9.2936	-116.4	152.8	697.8	19.78	1.99	2.18	26	21

Table 8.2. Data corresponding to the different *NVT* Seeding simulations performed in this work. See main text for the meaning of the different reported parameters.

Cavitation rate: Brute Force vs Seeding

In Fig. 8.5 we plot the rate versus the liquid pressure as obtained from Brute Force simulations (blue squares) and from Seeding (black and red circles using R_G and R_{ed} as definitions for the critical radius respectively). More than 300 orders of magnitude of the nucleation rate are spanned by our data. Brute Force data cover the highly negative pressure regime, where cavitation is spontaneous in the simulation time, whereas Seeding is used to obtain rate estimates in a higher pressure regime, where the rate is much lower and nucleation does not spontaneously occur. As discussed later on, the Seeding regime is more relevant to experiments.

The Gibbs radius systematically gives smaller rates than the equi-density one (by about 4-5 orders of magnitude) given that the nucleation barrier is proportional to the cubed bubble radius (Eq. (8.6)) and $R_G > R_{ed}$. An extrapolation to low pressures of the fits to Seeding data (done by linearly extrapolating the $\gamma(p)$ fits shown in Fig. 8.6(a)) suggests that by using R_{ed} as radius definition a better consistency with Brute Force is achieved (see the enlargement shown in Fig. 8.5 b)). We stress that the Brute Force rate is exempt from theoretical approximations. In this respect, R_{ed} seems to be a better definition than R_G of the critical bubble radius, R_c in the CNT expressions given by Eqs. (8.6) to (8.8).

In Fig. 8.7 we plot the Gibbs free energy barrier, ΔG_c , computed according to Eq. (8.6), from our Seeding simulations (dots) fitted via the linear $\gamma(p)$ dependence found in Fig. 8.6. The predicted free energy barrier height in the spontaneous cavitation pressure range (-750 to -650 bar) goes from 15 to 20 $k_B T$ according to the R_{ed} radius definition. These barrier heights are typical of spontaneous nucleation events in simulations [67, 49]. This consistency further demonstrates the match between Brute Force and Seeding extrapolated via the $\gamma(p)$ linear dependence of the data obtained with the equi-density radius definition.

Comparison with experiments

Experimental studies of cavitation, rather than having direct access to the nucleation rate, detect the thermodynamic state point at which a liquid water sample undergoes cavitation. In Fig. 8.8 the cavitation pressure is plotted against temperature. Empty and solid symbols correspond to experimental measurements and simulations respectively. Lines correspond to theoretical predictions.

We compare first our data against experiments of isobaric superheating [12] and isochoric cooling, the latter performed with quartz inclusions [1, 15]. The cavitation rate probed in these experiments, J_{exp} , is determined by the product of the employed volumes and observation times and ranges from 10^{10} to $10^{15}(\text{m}^{-3}\text{s}^{-1})$ [1, 19, 15, 68]. Therefore, in order to compare our simulations against experiments, we have to find the pressure range that gives the aforementioned rates (indicated with dotted horizontal lines in Fig. 8.5). By using this strategy of identifying iso-rate lines we were able to satisfactorily predict with simulations the

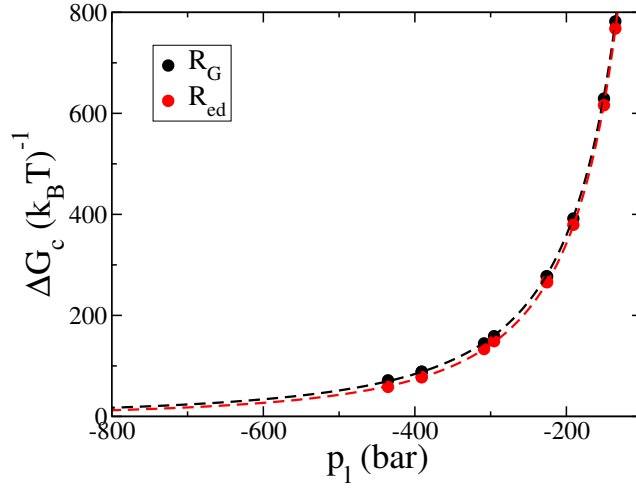


Figure 8.7. Gibbs free energy as a function of the liquid pressure from Seeding simulations considering the equi-density radius definition. 450 K. Black (red) circles are data obtained using the Gibbs (equi-density) radius definition. Dashed curves are fits based on the linear $\gamma(p)$ dependence shown in Fig. 8.6.

location of the so-called homogeneous ice nucleation line in studies of ice nucleation [69].

Using the $J(p)$ curves in Fig. 8.5 we can estimate by interpolation that cavitation in the experiments mentioned in the previous paragraph will occur between $p(J = 10^{10} \text{ m}^{-3} \text{ s}^{-1}) = -41 \text{ MPa}$ and $p(J = 10^{15} \text{ m}^{-3} \text{ s}^{-1}) = -44 \text{ MPa}$ at 450 K (we used the R_{ed} radius definition for this estimate, but the values obtained using R_G are very similar). This pressure range is quite narrow due to the large slope of the $J(p)$ curve. Such pressure range is our simulation estimate for the occurrence of cavitation in experiments of isobaric superheating or isochoric cooling (in quartz inclusions) at 450 K, and is indicated with a red dot for R_{ed} and with a black dot for R_G in Fig. 8.8 (the size of the dot includes the values of $p(J = 10^{10} - 10^{15} \text{ m}^{-3} \text{ s}^{-1})$). It is worth pointing out that at the pressures where we predict cavitation to occur in experiments (-41 to -44 MPa) we obtain a ΔG_c of 60 - $70 k_B T$ from the fit to the R_{ed} data shown in Fig. 8.7. These barrier heights are typical of nucleation experiments.

The dot in Fig. 8.8 obtained from our simulations at 450 K lies in the low pressure limit of the rather scattered experimental data cloud (blue empty diamonds) found around 450 K. This is consistent with the hypothesis that, around this temperature, there might be heterogeneous cavitation in the experiments [1], which is a pathway that leads to bubble nucleation at higher pressures than its homogeneous counterpart. Our simulation point, obviously, corresponds to homogeneous nucleation, which is why it stands close to the lowest attainable experimental pressures.

At high temperatures the experimental data are not scattered any more and they all nicely fall into a neat line. In order to compare our simulations with

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experiments in such temperature regime we performed extra *NVT* Seeding simulations at 550 K. The simulation details are identical to those described for 450 K except that we used a lower integration time step, namely 1 fs. At 550 K, we find a coexistence pressure of (39 ± 1) bar and an interfacial free energy of $(17 \pm 2) \text{ mJ m}^{-2}$, both consistent with Ref. [60] (38.01 bar) and Ref. [61] (38.3 bar and 17.4 mJ m^{-2}).

We run first a bubble of radius about 3 nm. We observe that the interfacial width at 550 K doubles that of 450 K (2 vs 1 nm). In equilibrium at 550 K, the bubble is surrounded by a liquid of $p = -73.2$ bar. Since its corresponding rate, $J = 10^7 \text{ m}^{-3} \text{ s}^{-1}$ (with the R_{ed} radius criterion), turned out to lie below the J range relevant to experiments, 10^{10} - $10^{15} \text{ m}^{-3} \text{ s}^{-1}$, we decided to equilibrate a couple of smaller bubbles in order to enable the interpolation. The rates calculated from the three Seeding runs are reported in Table 8.2 and are represented as empty circles in Fig. 8.5 (the kinetic pre-factor, that can be obtained with the data of the table using Eq. (8.7), is of the same order of magnitude as that found at 450 K: $10^{40} \text{ m}^{-3} \text{ s}^{-1}$). The $\gamma(p)$ dependence shown in Fig. 8.6b) is used to fit the $J(p)$ data at 550 K (dashed lines through empty circles in Fig. 8.5). By interpolation, we estimate that cavitation at 550 K will take place between -7.6 MPa and -8.5 MPa (using the R_{ed} radius definition). This pressure interval is included as a red dot in Fig. 8.8 and is quite close to the experimental line, which highlights the ability of the TIP4P/2005 model, in combination with the Seeding technique, to predict and justify the experimental cavitation behaviour. In Fig. 8.8 we also include two low temperature data coming from inclusion experiments (pink empty diamond [15]) and simulations (purple solid circle [3]). Again, simulations and inclusion experiments seem to be fully consistent with each other.

To summarise, our simulations seem to be in good agreement with superheating [12] and with quartz inclusions experiments [1] at high temperatures and those of Ref. [3] are consistent with more recent quartz inclusions experiments performed at lower temperatures [15]. We include in Fig. 8.8 a spline fit (red dotted line) to the three available simulation data (450 and 550 K from this work and 296.4 K from ref [3]) to give a visual idea of the cavitation line predicted by the TIP4P/2005 model. A direct comparison between the model and the experiment is enabled by the fact that TIP4P/2005 predicts quite well the critical temperature and the vapour pressure [60]. The model seems to mildly overestimate the cavitation pressure, which indicates that TIP4P/2005 overestimates the nucleation rate. Such overestimation could be due to the model having a smaller γ than real water [61]. Also, it should be taken into account that γ is very sensitive to the employed cutoff and that using larger cutoff distances could improve the agreement between simulation and experiment [61, 70]. In any case, the model predictions shown in Fig. 8.8 are already very satisfactory.

However, the scenario is not fully clear yet: measurements of the cavitation pressure with other strategies, like the Berthelot, centrifuge, acoustic cavitation and artificial tree techniques, indicated with empty symbols of different colours forming a cloud located at around -25 MPa and between 0 and 25°C , do not

agree with the trend set by our simulations and those of Ref. [3]. All these experiments find cavitation pressures well above those predicted by the simulations. In acoustic cavitation experiments, according to Ref. [35], the accessible rate is of the order of $10^{20} \text{ m}^{-3} \text{ s}^{-1}$. This is 5 orders of magnitude higher than the highest value we have used in this paper (and in Ref. [3]) to compare with inclusion experiments. However, if we had used a $10^{20} \text{ m}^{-3} \text{ s}^{-1}$ rate we would have found an even larger discrepancy because we would have predicted a lower cavitation pressure (pressure goes down as the rate goes up). Hence, we are unable to explain the discrepancy with acoustic cavitation experiments. What about Berthelot experiments? In such experiments isochoric cooling is performed as in quartz inclusions but in much larger volumes (about 5 orders of magnitude larger, 10^{-10} vs 10^{-15} m^3) [16]. Also the observation time is longer in Berthelot experiments (10^4 vs 10 s). With these time and volume scales, rates as low as $10^5 \text{ m}^{-3} \text{ s}^{-1}$ could be probed in Berthelot experiments. Inferring the cavitation pressure from $J=10^5 \text{ m}^{-3} \text{ s}^{-1}$, which is 5 orders of magnitude below the lower rate bound here considered, would go in the right direction, although it is not enough: both in our work at 450 K and in that of Ref. [3] at 296.4 K one can see that, in the experimentally relevant region (that given by the dotted lines in Fig. 8.5), the pressure barely changes 3 MPa every 5 orders of magnitude change of the rate. This is clearly insufficient to explain the $\sim 100 \text{ MPa}$ difference between simulations and Berthelot experiments shown in Fig. 8.8. Possibly, the explanation for such a large discrepancy between simulations and Berthelot or other sorts of experiments is that cavitation occurs at large pressures via heterogeneous nucleation in these experiments.

Finally, in Fig. 8.8 we also include the capillarity approximation prediction for the cavitation pressure in isobaric superheating or quartz inclusion experiments (green upward triangles). These triangles lie at lower pressures than circles corresponding to Seeding predictions. This is justified as follows. We have already discussed in Fig. 8.5 that the rate obtained from the capillarity approximation is lower than that coming from Seeding due to the decrease of γ as the bubble radius diminishes (see Fig. 8.6). Since the capillarity rate is lower, the pressure at which capillarity predicts a certain rate is lower too. However, it is perhaps surprising that the capillarity approximation prediction for the cavitation pressure is quite close to that obtained by Seeding despite the fact that capillarity rates lie 5-10 orders of magnitude below Seeding (see Fig. 8.5). Again, this is explained by the steep $J(p)$ curve in the experimentally relevant region (large rate changes correspond to rather small pressure variations). This justifies the proximity between Seeding and capillarity predictions of the cavitation pressure and between different theoretical approaches shown in Fig. 8.8 disregarding [25, 1] or taking into account [20] the variation of the interfacial free energy with pressure.

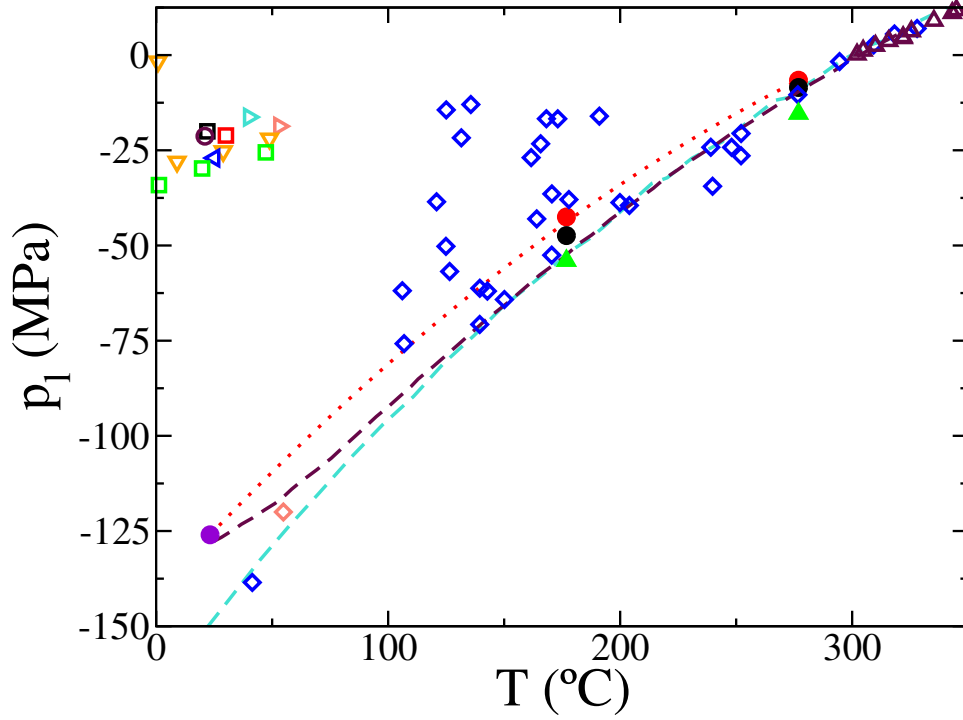


Figure 8.8. Cavitation pressure as a function of temperature obtained with experiments (empty symbols), simulations (filled symbols) and theory (dashed lines). Black and red filled dots correspond to our Seeding simulation predictions using R_G and R_{ed} as the radius definition respectively, whereas the purple dot corresponds to transition sampling simulations [3]. The dotted line is a spline fit to simulation data to help visualise the trend predicted by TIP4P/2005. Filled green up triangles are predictions combining simulation equations of state with the capillarity approximation (see main text). The cyan dashed line is a CNT-like prediction from Refs. [25, 1] and the maroon one is a density functional approach [20]. Blue [1] and pink [15] empty diamonds correspond to inclusion isochoric cooling experiments. Empty maroon up triangles are data from isobaric superheating experiments [12]. Right triangles correspond to Berthelot isochoric cooling experiments, in pale blue [16] and in pink [17]. Centrifuge experiments are represented with orange down triangles [71], shock wave experiments with blue up triangles [72], acoustic experiments with squares, in black from Ref. [14], in red from Ref. [37] and in green from Ref. [36]. The maroon circle is obtained using artificial trees [18].

8.5 Summary and conclusions

We investigate water cavitation with molecular dynamics simulations using the TIP4P/2005 model. Our first goal is to establish the cavitation rate versus pressure curve at 450 K. For that purpose we first evaluate the coexistence properties by simulating the liquid in contact with the vapour phase in direct coexistence. We find that the coexistence pressure is 4.49 bar and that the interfacial free energy is $(40 \pm 1) \text{ mJ m}^{-2}$. We then simulate the liquid at large negative pressures until we

find a regime where vapour bubbles spontaneously form in the course of an unbiased simulation. Due to the small size of the simulation volumes as compared to experimental ones this regime is found at very low pressures: below -650 bar. In such simulations we can estimate the nucleation rate by computing the average time required for a bubble to appear in the simulated liquid volume. We find nucleation rates in the range of $10^{30} - 10^{33} \text{ m}^{-3} \text{ s}^{-1}$ when lowering the pressure from -650 to -750 bar. We cannot simulate lower pressures because there is no longer an induction period before the appearance of a bubble. To compute the nucleation rate at larger pressures, which are more relevant to experiments, we resort to the Seeding method, which consists in simulating a bubble surrounded by liquid in the NVT ensemble, in our case at 450 K. In such simulations we compute the average pressure of the surrounding liquid with the virial expression and the bubble radius by means of radial density profiles (equi-density criterion). Alternatively, the radius is estimated using the definition of the equi-molar Gibbs dividing surface, which only requires knowing the volume of the simulation box, the total number of molecules, the liquid density and the vapour density. To obtain the latter we use thermodynamic integration of the equation of state of both phases, previously obtained with bulk phase simulations, and impose the condition of homogeneous chemical potential throughout the system. The vapour density thus obtained is consistent with that inferred from the density profile. This is expected in vapour-liquid transitions, but is not generally true in solid-liquid equilibrium [50, 51]. We combine the aforementioned simulation information (pressure of both phases, and bubble radius) with CNT to obtain estimates of the nucleation rate and the interfacial free energy. We get a huge variation of the nucleation rate (from 10^{-300} to $10^{10} \text{ m}^{-3} \text{ s}^{-1}$) in the pressure range going from -130 to -430 bar. The interfacial free energy goes down from its coexistence value as pressure goes down. The Gibbs radius definition predicts an interfacial free energy drop of $\sim 0,5 \text{ mN/m}$ per 100 bar decrease whereas the equi-density definition predicts approximately double that. Both criteria to identify the bubble radius give a similar rate trend although the Gibbs criterion gives lower values because it predicts higher interfacial free energies. By fitting the variation of the interfacial free energy with pressure to a straight line we can fit the rate data obtained with Seeding. We find that the fit to the Seeding data obtained with the equi-density radius definition extrapolates better to the regime where we computed the nucleation rate with unbiased simulations. Thus, the equi-density radius seems to be more appropriate to describe water cavitation with CNT. The γ variation with curvature obtained with the equi-density radius is fitted by a 0.1 nm Tolman length. We also compare the Seeding rate curves with that obtained using the capillarity approximation, i.e. by assuming that the interfacial free energy does not vary with pressure. Obviously, the capillarity curve predicts lower rates because it does not take into consideration the lowering of the interfacial free energy when moving away from coexistence. Finally, we compare our results with experiments. The experimental data available at 450 K are rather scattered so we decided to run a few extra Seeding simulations at 550 K where there are cleaner data. To compare with experiments we need to

8. The water cavitation line as predicted by the TIP4P/2005 model

predict the pressure at which the system undergoes cavitation at a given temperature. We do this prediction by interpolating in our rate vs pressure curves the rate at which it is expected that cavitation takes place in the experiments. With this strategy we get a successful comparison with both isobaric heating and isochoric cooling experiments with small volumes (quartz inclusions). However, we find irreconcilable discrepancies with the cavitation pressures obtained with other experimental techniques like Berthelot or acoustic cavitation. We hypothesise that there could be heterogeneous bubble nucleation in such experiments given that cavitation occurs at much higher pressures than predicted by our simulations and those of Ref. [3], performed at 296.4 K. Overall, our work shows an efficient manner to investigate and understand the factors that control and affect water cavitation using molecular simulations.

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Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

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9.1 Abstract

The liquid-vapour transition starts with the formation of a sufficiently large bubble in the metastable liquid to trigger the phase transition. Understanding this process is of fundamental and practical interest, but its study is challenging because it occurs over timescales that are too short for experiments but too long for simulations. The Seeding method estimates cavitation rates by simulating a liquid in which a bubble is inserted, thus avoiding the long times needed for its formation. In one-component systems, in the NpT ensemble the bubble grows or redissolves depending on whether its size is larger or smaller than the critical size, whereas in the NVT ensemble the critical bubble can remain in equilibrium. Provided that a good criterion is used to determine the bubble size, this method, combined with Classical Nucleation Theory (CNT), gives cavitation rates consistent with those obtained by methods independent of CNT. In this work, the applicability of NVT Seeding to homogeneous cavitation in mixtures is demonstrated, focusing on a partially miscible symmetrical binary Lennard-Jones (LJ) liquid at a temperature within the mixing regime. At the same stretching pressure, cavitation rates are higher in the binary than in the pure liquid due to the lower interfacial free energy of the mixture. Curiously, the cost of creating a bubble is similar in the pure and binary LJ liquids at the same metastability, $\Delta\mu/\Delta\mu_{spin}$, with $\Delta\mu$ being the diffe-

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rence of chemical potential between the metastable liquid and coexistence, and $\Delta\mu_{spin}$ between the spinodal and coexistence.

9.2 Introduction

Understanding the formation of bubbles from metastable liquids is a problem of high interest in many fields, such as sonochemistry[1] or geology [2]. Experiments often provide information about the cavitation rates, i.e, about the number of bubbles formed per unit of time and per unit of volume, but not about the microscopic mechanism that leads to their formation. With the aim of understanding this process, Classical Nucleation Theory [3, 4] (CNT) was proposed a century ago, initially to rationalise the condensation of supersaturated vapours, but later it was also applied to other transitions, including the cavitation of bubbles [5].

Molecular simulations have also been extensively used to study the nucleation of bubbles [6, 7, 8, 9, 10, 11, 12, 13, 14]. Experiments are often performed at conditions in which the nucleation rates are too low as compared with the typical simulation times, thus, special simulation techniques, such as Umbrella Sampling [15, 16, 17, 18], Forward-Flux sampling [6, 19, 7] or Transition Path Sampling [20, 21, 22] have been employed. Even though these methods are rigorous, they are often technically challenging and computationally demanding. As an alternative, during the last years the Seeding method has been gaining popularity, mainly due to the lower computational cost and easier implementation than the preceding methods, with focus not only in bubble cavitation [9, 10, 11, 13] but also on other transitions, such as crystallisation or condensation [23, 24, 25, 26, 27]. This method consists in inserting a seed of the stable phase within the metastable liquid, and searching for the conditions for which the inserted seed is critical, i.e., it stands at the top of the free energy barrier that separates the metastable and stable phases. For one-component systems, this method can be implemented both in the NpT ensemble, in which the critical nucleus is in unstable equilibrium, or in the NVT ensemble in which is in stable equilibrium, thus enabling the study of the properties of the critical cluster over longer times [10, 11, 13]. The information of the critical cluster size is then combined with expressions from CNT to calculate the cavitation rates. The application of NVT and NpT Seeding to study the cavitation of bubbles in the truncated and force-shifted Lennard-Jones (TFS-LJ) liquid has provided rates consistent with those obtained from other simulation techniques that do not depend on CNT [9, 10, 11].

The main goal of this article is to extend the method of NVT Seeding to study the nucleation of bubbles in binary systems. The applicability of NVT Seeding has been already demonstrated for other transitions besides cavitation, in particular for crystal nucleation, but always for one-component systems [28]. NpT Seeding was not used either to study bubble nucleation in multi-component systems, but it has been successfully applied to study nucleation of crystals in several multi-component systems, such as, for example, crystallisation of NaCl and ice

from aqueous solutions [29, 30, 31] and nucleation of methane hydrates [32]. In this work, the applicability of *NVT* Seeding to multi-component systems will be investigated by studying bubble nucleation in a partially miscible binary symmetrical LJ mixture. This is one of the simplest mixtures one can think of, and this makes it an ideal model system in which to investigate the applicability of *NVT* Seeding before addressing nucleation in more complex binary systems.

Simulation studies of cavitation of bubbles from binary mixtures are rather scarce and often this phenomenon has been studied theoretically, for example, in the framework of density functional theory or in the framework of CNT [33, 34, 35, 36]. However, the extension of CNT to multi-component systems has not been straightforward [37, 38, 39]. Several of the proposed formulations lead to unphysical results, specially for non-ideal mixtures, which has been ascribed to the fact that the effect of the curvature in the interfacial free energy cannot be neglected [39]. The nucleation of bubbles in binary mixtures is very rich and involves many different scenarios depending on the interaction parameters. Curious phenomena have been found, such as for example, an anomalous decrease of the nucleation rate when temperature increases at constant pressure in mixtures of species of different volatility [34]. However, as our main goal is to illustrate the applicability of *NVT* Seeding, we will focus on the case of a partially miscible symmetrical LJ mixture at a temperature at which the liquid is miscible. In these conditions, we expect that the cavitation behaviour follows a similar mechanism as that in the pure system.

9.3 Methods and simulation details

9.3.1 Model

The model system is a binary symmetrical mixture of equal-sized spheres. The interaction between any pair of molecules is described by the truncated and force-shifted Lennard-Jones model (TSF-LJ) [6]:

$$U_{TSF-LJ}(r) = U_{LJ}(r) - U_{LJ}(r_c) - (r - r_c)U'_{LJ}(r_c) \quad (9.1)$$

where r is the distance between two molecules, $U_{LJ}(r)$ is the standard 12-6 LJ potential and $U'_{LJ}(r)$ its first derivative, and $r_c = 2.5\sigma$ is the cut-off distance. We have chosen this short ranged model to avoid dealing with long range corrections which are problematic in heterogeneous systems with large variations in density, as the liquid-bubble systems considered in this work. Besides, there are numerous studies of cavitation in the pure TSF-LJ that can be compared with the results for the binary symmetrical mixture [6, 7, 9, 10, 11]. Here we consider a mixture of spheres with equal size, $\sigma_{AA} = \sigma_{BB}$, and equal mass $m_A = m_B$.

The phase diagram of partially miscible symmetrical TSF-LJ mixtures ($\sigma_{AA} = \sigma_{BB} = \sigma_{AB} \equiv \sigma$ and $\epsilon_{AA} = \epsilon_{BB} \equiv \epsilon$, and ϵ_{AB}/ϵ less than, but close to 1) has not

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yet been reported to the best of our knowledge. However, for the standard LJ potential, the global phase diagram (which delimits regions of parameter space with the same phase diagram topology) has been calculated [40] from the equation of state proposed by Johnson *et al* [41]. These authors found that symmetrical LJ mixtures with $\epsilon_{AB}/\epsilon > 0.75$ exhibit a type II diagram according to Bolz's classification [42]. This means that in a pressure versus temperature projection, at low temperature there is liquid-liquid-vapour three coexistence line that, as T increases, transforms first in a critical azeotropic line and then in a critical liquid-vapour line. According to Ref. [40], for a mixture with $\epsilon_{AB}/\epsilon = 0.8$, $T^* = k_B T/\epsilon = 0.785$ (which is the T^* for which cavitation was studied for the pure TSF-LJ liquid in previous works [10, 11, 12]) falls within the mixing region. As our intention is to study cavitation of bubbles from a homogeneous binary liquid mixture, we set $\epsilon_{AB}/\epsilon = 0.9$, so that the liquid does not undergo demixing at the considered T^* . In the Seeding simulations performed in this work, the concentration of the liquid is set to the molar fraction $x_{A,l} = 0.75$, where the subscript l is added to differentiate the composition of the liquid from that of the bubble.

Molecular Dynamics simulations were performed with the GROMACS 4.6.7 package (double precision) [43]. To implement the chosen model system, we used the argon parameters, i.e., the diameter of the particles is set to $\sigma = 3.405 \text{ \AA}$, the energy parameter to $\epsilon = 0.996078 \text{ kJ mol}^{-1}$ and the mass is $m = 39.946 \text{ u}$. In the remaining of this article, all the quantities will be presented in LJ reduced units: the volume $V^* = V/\sigma^3$, the density $\rho^* = (N/V)\sigma^3$ (N is the number of particles in the system), the temperature $T^* = k_B T/\epsilon$, the pressure $p^* = p\sigma^3/\epsilon$ and the time $t^* = t/\tau$, with $\tau = \sqrt{m\sigma^2/\epsilon} = 2.156 \text{ ps}$. In these units $p^* = 1$ corresponds to $p = 419 \text{ bar}$.

The pressure was controlled using an isotropic Parrinello-Rahman barostat [44], with a relaxation time of $t = 2 \text{ ps}$ ($t^* \approx 0.92$) and a compressibility of $7 \times 10^{-5} \text{ bar}^{-1}$. For temperature coupling, velocity rescaling was used with a stochastic term [45] and with a relaxation time of $t = 1 \text{ ps}$ ($t^* \approx 0.46$). The temperature was fixed at $T^* = 0.785$. The equations of motion were integrated using the velocity-Verlet algorithm with a time step of $t = 0.005 \text{ ps}$ ($t^* \approx 0.002$).

9.3.2 Classical Nucleation Theory and the Seeding method

According to CNT, the nucleation rate, i.e., the number of nuclei of the stable phase that form in the metastable phase per unit of volume and per unit of time, at constant pressure, temperature and composition, can be calculated from [3, 4, 46, 37, 39, 47]:

$$J = K \exp\left(\frac{-\Delta G_c}{k_B T}\right) \quad (9.2)$$

where k_B is the Boltzmann constant, ΔG_c is the Gibbs free energy barrier for the formation of a critical bubble and K is the kinetic prefactor. ΔG_c can be computed as:

$$\Delta G_c = -V\Delta p + \gamma A \quad (9.3)$$

where V and A are, respectively, the volume and the area of the surface of the critical bubble, γ is the interfacial free energy of the critical bubble and $\Delta p = p_{bubble} - p_l$ is the difference of pressure between the critical bubble and the surrounding liquid. Assuming a spherical critical bubble of radius R_c , and using Laplace equation:

$$R_c = \frac{2\gamma}{\Delta p}, \quad (9.4)$$

the free energy barrier can also be expressed as:

$$\Delta G_c = \frac{2\pi \Delta p R_c^3}{3}. \quad (9.5)$$

Note that this expression for ΔG_c is formally identical to that for pure systems [46, 9]. The main difference with respect to mono-component systems is the procedure used to calculate Δp . In equilibrium, the chemical potential of the liquid and the bubble is the same. In previous studies of pure systems, the pressure inside the bubble was estimated by integrating the equation of state of a bulk vapour to find the pressure for which the chemical potential of the bubble is the same as that of the surrounding liquid [9, 10, 11]. This calculation is a bit more complex in the mixture, because we have to find the pressure and composition for which the chemical potentials of the two components are equal in both phases. It is also important to point out that the radius of the critical cluster R_c that enters in Eq. 9.5 is the one that satisfies Laplace equation (Eq. 9.4), i.e., the radius at the surface of tension where the value of γ is a minimum with respect to formal changes of the dividing surface [48]. The kinetic factor can be calculated from [46, 34]:

$$K = \rho_l \sqrt{\frac{\Delta p R_c}{\pi}} \left(\frac{x_{A,v}}{\sqrt{m_A}} + \frac{x_{B,v}}{\sqrt{m_B}} \right) \quad (9.6)$$

where m_A and m_B are the masses of the particles of type A and B, $x_{A,v}$ and $x_{B,v}$ are their vapour molar fractions, and ρ_l is the number density of the metastable liquid. In our system the mass of both particle types is the same ($m_A = m_B = m$), and the kinetic prefactor simplifies down to the same expression as that used for one-component systems [5]:

$$K = \rho_l \sqrt{\frac{\Delta p R_c}{m\pi}} \quad (9.7)$$

In the Seeding method [27], a spherical seed of the stable phase is inserted in the equilibrated metastable phase. For one-component systems, simulations of this heterogeneous system can be performed either in the NpT or NVT ensembles [10, 28]. In pure systems, the critical cluster corresponds to a maximum in G at constant N , p , T , and to a minimum in F at constant N , T and V (corresponding at the same p) [10, 49]. Thus, it is possible to have the critical bubble in stable equilibrium with the liquid, allowing to study its properties over longer times. The main

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goal of this paper is to show the applicability of *NVT* Seeding for binary systems. In our simulations the number of particles of each type are kept constant, so that, strictly speaking, we are working in the $N_A N_B VT$ ensemble or $NVT x_A$ ensemble, x_A being the overall molar fraction of component A. However, for simplicity, we will use the notation *NVT* (and *NpT*), keeping in mind that simulations are performed at constant overall composition. The critical bubble size obtained from Seeding will be used together with Eq. 9.5 to estimate the free energy barrier and the nucleation rate using Eq. 9.2. As the results of Seeding are very sensitive to the size of the critical cluster, it is extremely important to choose a criterion to determine the bubble sizes that gives rates consistent with those derived from methods that do not depend on it [9, 10]. In this work, we will use brute force simulations to test two criteria to define the bubble sizes.

9.4 Results

9.4.1 Liquid-vapour coexistence

The first step to study the cavitation in the symmetrical TSF-LJ mixture is to locate the liquid-vapour coexistence point at the chosen concentration, $x_{A,l} = 0,75$. To facilitate the comparison with cavitation in the pure TSF-LJ liquid, simulations are performed at the same reduced temperature as in previous works ($T^* = 0,785$) [10, 11]. The coexistence point was evaluated by two independent routes: by direct coexistence simulations [50, 51, 52], and by calculation of the chemical potential of the two components in the two phases and imposing the condition of phase equilibrium.

Direct coexistence simulations

In order to locate the liquid-vapour equilibrium using direct coexistence simulations, we first equilibrate a liquid composed of 2370 particles of type A and 790 particles of type B (i.e., a liquid with molar fraction $x_A = 0,75$) at $T^* = 0,785$ in the *NpT* ensemble. The approximate simulation box dimensions are $4,32 \times 4,32 \times 8,64$ nm. Once the liquid is equilibrated, we introduce an empty space next to the liquid of length about twice that its longer dimension (the size of the simulation box is $4,32 \times 4,32 \times 30$ nm when the empty space is inserted). This system is then allowed to evolve in the *NVT* ensemble.

Once the system reaches equilibrium, the coexistence pressure is estimated from the normal component of the pressure tensor, which for the conditions just described, is $p_{lv}^* = 0,0334(3)$. The equilibrium composition of each phase is calculated by measuring the total and partial density profiles along the direction perpendicular to the interface. We obtained that, after equilibration, the concentration of particles of type A in the liquid phase increased up to about $x_{A,l} = 0,77(1)$ and that of the gas phase decreased down to about $x_{A,v} = 0,69(1)$. This enrichment

of component A in the liquid phase can be easily understood by energetic arguments. As crossed interactions are lower than those between like particles, and interactions are much more relevant in the liquid than in the gas phase (in which particles are on average far away from each other), it is energetically favourable to reduce the number of crossed interactions in the liquid by releasing to the vapour a larger proportion of particles of type B.

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System	Method	T^*	p_{lv}^*	ρ_l^*	ρ_v^*	$x_{A,l}$	$x_{A,v}$	x_A	γ^*
Pure LJ	DC	0.785	0.0267(1)	0.665(2)	0.044(2)	–	–	–	0.196(4)
Pure LJ	DC [11]	0.785	0.0267	–	–	–	–	–	0.193
Pure LJ	DC [6]	0.785	0.026	0.668	0.043	–	–	–	0.204(7)
Symmetric LJ	DC	0.785	0.0334(3)	0.639(4)	0.059(4)	0.77(1)	0.69(1)	0.75	0.145(4)
Symmetric LJ (Big)	DC	0.785	0.0335(3)	0.639(4)	0.059(4)	0.76(1)	0.68(1)	0.75	0.145(4)
Symmetric LJ	DC	0.785	0.0336(3)	0.638(4)	0.059(4)	0.75(1)	0.67(1)	0.73	0.142(4)
Symmetric LJ	CP	0.785	0.0341(3)	–	–	0.75	0.67(1)	–	–

Tabla 9.1. Liquid-vapour equilibrium for the pure and the symmetric TSF-LJ mixture at $T^* = 0,785$ obtained by direct coexistence (DC) simulations and by computation of the chemical potentials (CP). ρ_l^* and ρ_v^* are the overall densities of the liquid and vapour at coexistence, and $x_{A,l}$ and $x_{A,v}$ are the molar fractions of component A in the liquid and in the vapour. x_A is the global molar fraction in the whole system, i.e. $x_A = N_A/(N_A + N_B)$, where N_A and N_B are the total number of molecules of type A and B in the simulation box. p_{lv}^* is the coexistence pressure, which in DC simulations is obtained from the normal component of the pressure tensor. γ^* is the liquid-vapour interfacial free energy and is given in LJ reduced units ($\gamma^* = \gamma\sigma^2/\epsilon$). The DC simulations labelled as Big were carried out in a larger system with 7110 particles of type A and 2370 particles of type B, in a box of $4,22 \times 4,22 \times 60$ nm.

As all the cavitation studies presented in this work were performed for a liquid with composition $x_{A,l} = 0,75$, we repeated the direct coexistence simulations to try to locate the liquid-vapour transition when the liquid has a composition closer to this value. As the concentration of A in the liquid, $x_{A,l}$, tends to increase when brought in contact with vacuum, we now start the direct coexistence simulations from a liquid phase containing 2323 particles of type A and 837 particles of type B, so that the initial composition of the liquid is $x_A = 0,735$, i.e. somewhat below the target $x_{A,l} = 0,75$. This system equilibrates at a slightly lower coexistence pressure than before, $p_{lv}^* = 0,0341(3)$, but with the desired liquid equilibrium concentration of A, namely, $x_{A,l}=0.75(1)$ and with $x_{A,v}=0.68(1)$ in the vapour. Finally, we also checked that the coexistence pressure coincides with that obtained using equations of state (EOS) of the bulk liquid and vapour phases together with the densities and compositions of the liquid and vapour phases extracted from the bulk region of each phase (i.e., sufficiently away from the interface) in the direct coexistence simulations. Using this procedure, we get $p_l^* = 0,033(1)$ from the EOS of the bulk liquid and $p_v^* = 0,034(1)$ from the EOS of the bulk vapour. Both values are in very good agreement with each other and also with the estimate from the normal component of the pressure tensor.

The interfacial free energy, γ , at coexistence can be calculated from the average pressure tensor: [53, 48, 54, 55, 56, 57, 58]

$$\gamma = \frac{L_z \left[\bar{p}_{zz} - \frac{\bar{p}_{xx} + \bar{p}_{yy}}{2} \right]}{2} \quad (9.8)$$

where L_z is the length of the simulation box in the direction normal to the interface, $\bar{p}_{zz}$ is the average of the normal component of the pressure and $\bar{p}_{xx}$ and $\bar{p}_{yy}$ are the averages of the tangential components of the pressure. The value of the average components of the pressure tensor do not depend on any particular formulation of the local pressure tensor [53, 57, 58]. The factor 2 in the denominator of Eq. 9.8 takes into account that two liquid-vapour interfaces are formed by the periodicity of the simulation box.

The coexistence conditions as well as the interfacial free energy for the TSF-LJ mixture are gathered in Table 9.1. For completeness, we also performed simulations for the pure TSF-LJ system at $T^* = 0,785$, and these results are compared with data from previous works [6, 11] in the same Table. The first observation is that the liquid-vapour coexistence and the interfacial free energy obtained by us for the pure system are fully consistent with those found in the literature. [6, 11] Comparing now the data for the pure and the symmetrical TSF-LJ mixture at the same temperature, it can be seen that the liquid-vapour coexistence pressure of the symmetrical mixture is higher than that of the pure TSF-LJ system, which is in keeping with the trends observed in Ref. [40]. Finally, the interfacial free energy is appreciably lower in the symmetrical TSF-LJ mixture than in the pure system. The same qualitative behaviour was found in previous work [59], but a quantitative comparison cannot be made as this work considered a mixture with a different composition ($x_A=0.5$) and used a different truncation of the interatomic potential.

Coexistence point from chemical potential calculation

An alternative method to calculate the liquid-vapour coexistence point is to find the thermodynamic conditions at which the chemical potential of the two components is equal in both phases at the same temperature T and at the same pressure p :

$$\begin{aligned}\mu_{A,l}(p, T, x_{A,l}) &= \mu_{A,v}(p, T, x_{A,v}) \\ \mu_{B,l}(p, T, x_{B,l}) &= \mu_{B,v}(p, T, x_{B,v})\end{aligned}\quad (9.9)$$

where $\mu_{i,\alpha}(p, T, x_{i,\alpha})$ and $x_{i,\alpha}$ are, respectively, the chemical potential and molar fraction of component i (i being A or B component) in phase α (α being the liquid or vapour phase).

The excess chemical potential of components A and B in a liquid mixture with $x_{A,l}=0.75$ and in the vapour with $x_{A,v}=0.60, 0.65$ and 0.70 as a function of pressure were calculated using the particle test Widom method [60, 61] as implemented in GROMACS [43]. For that aim, we performed NpT simulations of each phase in a cubic simulation box containing 1000 particles. Typically, the chemical potential was averaged over 2000 configurations, collected over a MD simulation run consisting of 2×10^7 steps, after reaching equilibrium. The total chemical potential was obtained by adding to the excess chemical potential the ideal contribution, which for component i is given by: $\mu_{i,id}/(k_B T) = \ln(x_i \rho \sigma^3)$, where x_i is its molar fraction. The thermal de Broglie length is the same in both phases and its value does not change the chemical potential difference between them. Here it was assigned to the arbitrary value σ .

The chemical potential of the two components in the liquid and vapour phases is shown in Fig. 9.1 (a). As can be seen, the chemical potential of component A in the liquid with $x_{A,l} = 0.75$ (black lines and symbols) crosses the chemical potential of component A in the vapour with concentrations $x_{A,v}=0.60$ (red), 0.65 (blue) and 0.70 (green) at decreasing pressures, and the opposite occurs for the minority component B (i.e., the chemical potential of the liquid crosses that of the gas phase at increasing pressures as $x_{A,v}$ increases). These crossing points fulfil the condition that the chemical potential of the corresponding component is equal in the liquid and in the vapour phases. The crossing points for each component can be represented as a function of the vapour composition, $x_{A,v}$, obtaining two lines, one for each component, with opposite slopes (see Fig. 9.1 (b)). Only at the crossing point between these two lines the equality of chemical potentials of each component occurs at the same composition of the vapour ($x_{a,v}$) and at the same pressure. From this we obtain that, at $T^* = 0.785$, the symmetrical TSF-LJ liquid with composition $x_{A,l} = 0.75$ coexists with the vapour phase with composition $x_{A,v} = 0.67(1)$ at $p_{lv}^* = 0.0341(3)$. As can be seen in Table 9.1 these results are in full agreement with those obtained by the direct coexistence route.

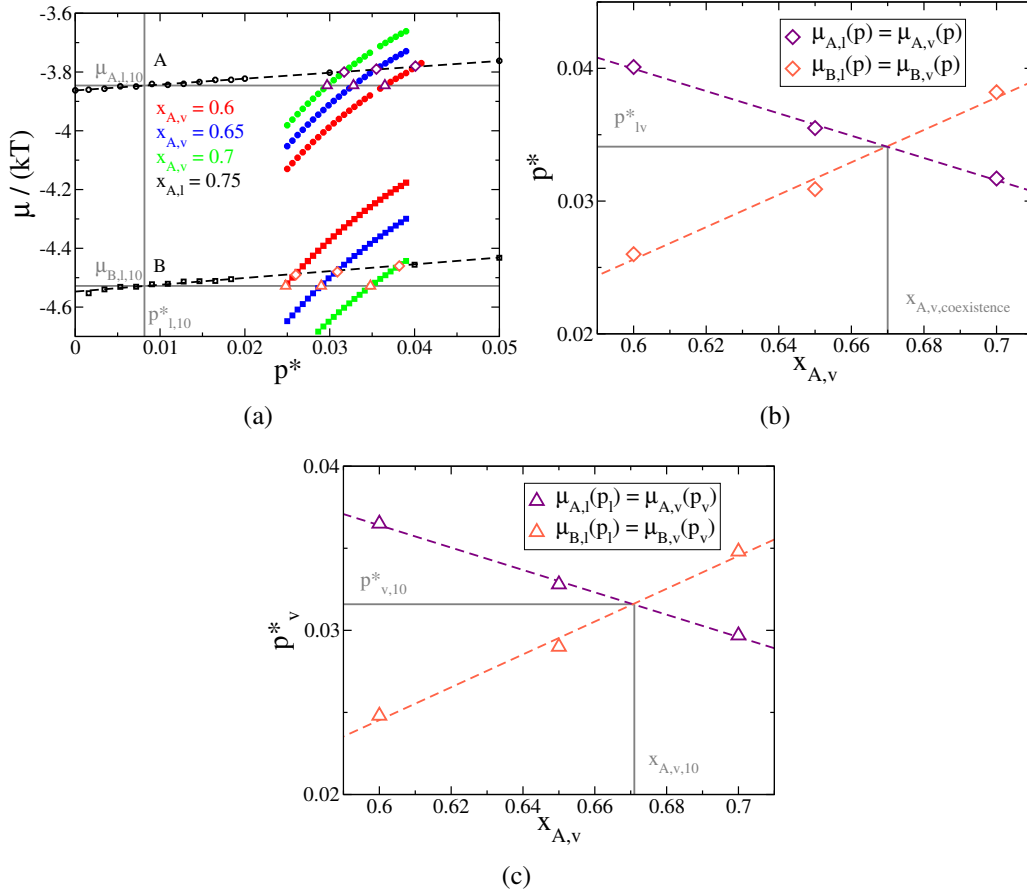


Figure 9.1. (a) Chemical potential versus pressure for component A (circles) and B (squares) in a symmetrical TSF-LJ mixture with $\epsilon_{AB}^* = 0.9$ at $T^* = 0.785$. Black symbols show data for the liquid with $x_{A,l} = 0.75$ (dashed lines are linear fits) and red, blue and green symbols show data for the vapour with $x_{A,v} = 0.6$, $x_{A,v} = 0.65$ and $x_{A,v} = 0.7$, respectively. (b) Estimation of the coexistence point. The points at which the chemical potential of each component in the liquid and vapour at different concentrations are equal are marked as diamonds (purple for A and pink for B) in (a) and presented jointly in (b). The crossing of these two lines gives the coexistence point. (c) Calculation of the pressure inside the bubble for system 10. The pressure and the chemical potential of the surrounding liquid are shown as a vertical and a horizontal grey lines in panel (a), respectively. Purple triangles mark the points at which the chemical potential of A in the vapour is the same as in the surrounding liquid, whereas red ones are the equivalent points for B. The crossing point of the two lines gives the equilibrium bubble-liquid conditions.

9.4.2 Cavitation rate via brute force simulations

As mentioned before, one of the difficulties of studying nucleation by Seeding is that this method depends critically on having a good criterion to estimate the size of the critical nucleus. Typically this problem has been sorted out by comparing the nucleation rates obtained with Seeding with those coming from more rigo-

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rous simulation techniques, such as Umbrella Sampling, Forward-Flux sampling or brute force simulations [27, 9, 10]. Given that we are not aware of previous estimates of the bubble cavitation rate for the symmetrical TSF-LJ mixture, we started by studying cavitation by brute force simulations. At high metastabilities the free energy barrier for nucleation decreases, and spontaneous cavitation becomes accessible within the typical length and time scales of simulations.

For that aim, we performed *NpT* simulations of a liquid with composition $x_{A,l}=0.75$, containing 18960 particles of type A and 6320 of type B. At these conditions we were able to observe spontaneous cavitation only at negative pressures. For each considered pressure, we ran 10 independent simulations. Cavitation events can be easily detected by an abrupt increase of density. The cavitation rate can be estimated from these simulations as:

$$J = \frac{1}{\langle t \rangle \langle V \rangle}, \quad (9.10)$$

where $\langle t \rangle$ is the average time for observing spontaneous cavitation, which is calculated simply as the average of the time for cavitation in the 10 independent simulations performed for each pressure, and $\langle V \rangle$ is the average volume of the simulation box before the cavitation event. We checked that 10 simulations are enough to obtain an accurate estimate of the nucleation rate with an error significantly lower than one order of magnitude, by comparing the rate obtained from 20 independent simulations with those obtained from only 10. The cavitation rates obtained by brute force simulations are given in Table 9.2.

p^*	$\langle t^* \rangle$	$\langle V^* \rangle$	J^*
-0.0300	$4.3(4) \times 10^2$	42380(20)	$5.5(5) \times 10^{-8}$
-0.0297	$2.6(7) \times 10^3$	42255(4)	$9(2) \times 10^{-9}$
-0.0235	$1.7(4) \times 10^4$	41993(3)	$1.4(4) \times 10^{-9}$
-0.0200	$2.9(6) \times 10^5$	41746.8(9)	$8(2) \times 10^{-11}$
-0.0177	$4(1) \times 10^6$	41599(2)	$6(2) \times 10^{-12}$

Table 9.2. Cavitation rate for the symmetrical TSF-LJ mixture with $\varepsilon_{AB}^*=0.9$ at $x_{A,l}=0.75$ and $T^*=0.785$ as obtained from brute force simulations. The rates are given in LJ reduced units ($J^* = J\sigma^3\tau$). For the three lower pressures, averages were performed over 20 independent simulations, whereas 10 simulations were used for the two higher pressures.

9.4.3 Cavitation rate via *NVT* seeding

As seen in Section 9.3.2, the estimation of the cavitation rate requires to calculate the free energy barrier ΔG_c and the kinetic prefactor K . The cavitation free energy barrier can be obtained from the size of the critical cluster, R_c , and the pressure difference between the bubble and the surrounding liquid, Δp (Eq. 9.5). In the next subsections, we will see how to estimate these properties. It is important to recall

that the expression of the free energy barrier ΔG_c , Eq. 9.5, was derived under the assumption that the composition of the metastable phase remains constant during the bubble nucleation. This is true in the thermodynamic limit where the size of the critical bubble is negligible compared to the size of the system (so that the formation of the bubble causes only an infinitesimal change in the composition of the external liquid phase). In previous studies of nucleation of droplets and crystals from binary mixtures, simulations were performed in the isothermal-isobaric semigrand ensemble (in which p , T , N and the chemical potential difference between the two species are kept constant) [18, 62, 47]. As will be shown later, in the liquid-bubble simulations performed in this work, the composition of the liquid remains almost unchanged. The reason is that, even though the composition of the bubble is different from that of the metastable liquid, the number of particles in the bubble is so small compared to that in the surrounding liquid that it barely changes its composition. Therefore, the use of the NVT ensemble, keeping the overall composition constant, is justified in this case.

Estimation of the radius of the critical cluster, R_c

The protocol used to construct initial configurations of the liquid in coexistence with bubble is as follows. First, we equilibrate the liquid with composition $x_{A,l}=0.75$ by performing NpT simulations at $T^*=0.785$. In order to be able to accommodate bubbles of different sizes, we considered two system sizes, a smaller one with $N=10000$ particles and another one with $N=130000$ equilibrated during 1 million MD steps. Bubbles of different sizes are then generated by removing all the particles from a spherical region defined in the equilibrated liquid simulation box. The sizes of the bubbles were chosen so that the ratio between the volumes of bubble and simulation box was within 5-15 % (see Table 9.3). Previous work suggests that within these limits Seeding simulations are not significantly affected by finite size effects [9].

These systems containing the artificially constructed bubbles are then allowed to evolve in the NVT ensemble for 2×10^6 MD steps. Initially bubbles grow or shrink until an equilibrium with the surrounding liquid is established. Note that not all the bubbles will equilibrate, depending on the choice of the total number of particles, size of the simulation box and total density [63]. In those systems in which the bubble remains stable after equilibration, i.e. it does not completely dissolve in the timescale of our simulation, we estimate their average radius in simulations consisting of 100-400 million MD steps.

As mentioned before, in Seeding, nucleation rates can change significantly depending on the criterion used to define the cluster size [9, 29]. The radius that enters in CNT is that given by the surface of tension, i.e., the surface in which the surface tension acts [64, 65, 48, 63]. However, the location of that interface is not known [66, 67]. For that reason, in previous implementations of the Seeding method, the radius of the critical nucleus is estimated using a criterion that yields nucleation rates consistent with those obtained from rigorous simulations that do

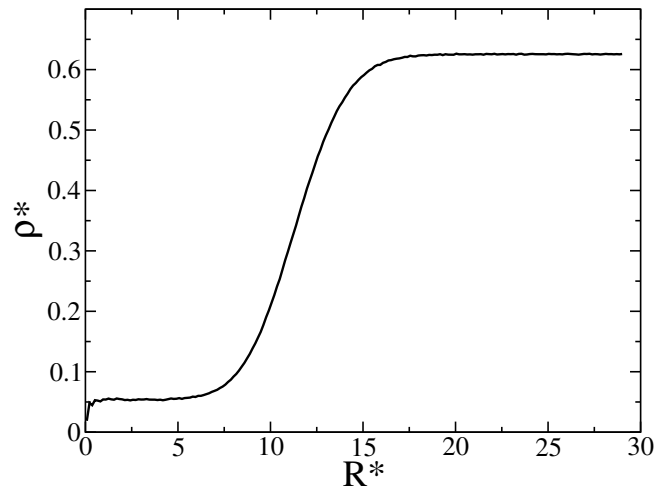
9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

not depend on the critical cluster size, such as Umbrella Sampling or brute force simulations [31, 9, 11].

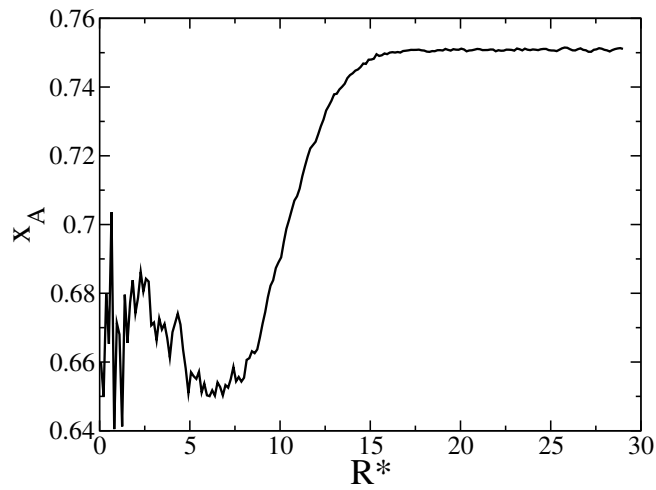
Here we employed two criteria used in previous works to define the bubble size [9, 11]. Later we will compare the cavitation rates derived from these two alternative criteria to see which one gives results in closer agreement with those from brute force simulations. In the first criterion, the radius of the bubble is taken as the equidensity radius, [9] which is defined as the distance at which the density is equal to the average of the liquid and gas densities measured sufficiently away from the interface (where radial densities remain constant). The equidensity radius is estimated from the radial overall density profile measured from the centre of the bubble, as shown in Fig. 9.2 (a). Following previous work [10], the centre of the bubble in each instantaneous configuration is located by searching for the positions of the minima in the density profiles calculated along the x , y and z directions using a bin width of about 0.7σ . The radial density profile is calculated using a bin of width 0.15σ in the radial direction and is typically averaged over 1000 independent configurations stored every 20000 steps, so that the typical length of the simulations used for these calculations is 20 million MD steps. The radial overall density profile is then fitted to the following sigmoid function:

$$\rho(r) = \frac{\rho_{v,dp} + \rho_{l,dp}}{2} + \left(\frac{\rho_{l,dp} - \rho_{v,dp}}{2} \right) \cdot \tanh[(r - R_c) / \alpha] \quad (9.11)$$

that has four fitting parameters: $\rho_{v,dp}$ and $\rho_{l,dp}$ provide estimates of the densities of the vapour and the liquid phases (the subscript dp stands for density profile), α is a measure of the width of the interfacial region, and R_{ed} is the distance at which the density adopts the average liquid and vapour densities. The values for $\rho_{v,dp}$ and $\rho_{l,dp}$ obtained from this fit are coherent (within their statistical uncertainty) with the values inferred from averaging the density profiles of the vapour and the liquid region, respectively, in Fig. 9.2. Notice that the error in the estimation of the vapour density $\rho_{v,dp}$ is higher than that of the liquid density $\rho_{l,dp}$ since there are only a few particles in the bubble, resulting in large fluctuations in the density.



(a)



(b)

Figure 9.2. a) Radial overall density profile and b) radial concentration profile for the system labelled with the index 10 in Table 9.3. $R^* = R/\sigma$ is the radial distance to the bubble center.

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

Index	N_A	N_B	p_l^* $\pm 0,0001$	Δp^* $\pm 0,0002$	ρ_l^* $\pm 0,0002$	ρ_v^* $\pm 0,0003$	$x_{A,v}$ $\pm 0,001$
0	6706	2239	-0.0156	0.0448	0.6110	0.0485	0.676
1	18173	6074	-0.0083	0.0383	0.6155	0.0503	0.673
2	17636	5852	-0.0068	0.0370	0.6163	0.0507	0.673
3	17187	5727	-0.0022	0.0328	0.6191	0.0518	0.672
4	17918	5973	-0.0019	0.0326	0.6192	0.0519	0.672
5	17240	5738	-0.0004	0.0312	0.6201	0.0522	0.672
6	17605	5875	0.0014	0.0296	0.6211	0.0527	0.671
7	16788	5583	0.0033	0.0279	0.6222	0.0531	0.671
8	17319	5771	0.0034	0.0278	0.6223	0.0532	0.671
9	90900	30338	0.0031	0.0285	0.6221	0.0542	0.671
10	90108	30063	0.0082	0.0235	0.6249	0.0543	0.671
11	89191	29781	0.0107	0.0212	0.6263	0.0549	0.670
12	88274	29438	0.0123	0.0197	0.6272	0.0553	0.670
13	87290	29072	0.0136	0.0185	0.6279	0.0555	0.670
14	86219	28712	0.0147	0.0175	0.6285	0.0558	0.670
15	85044	28330	0.0157	0.0166	0.6290	0.0560	0.671
16	82545	27468	0.0172	0.0153	0.6297	0.0563	0.671
17	79572	26512	0.0184	0.0142	0.6303	0.0566	0.671

Table 9.3. Details of the systems for which bubbles in equilibrium with the liquid phase were obtained in *NVT* simulations. Each system is labelled with a numerical index for further reference. Besides the total number of particles of each type (N_A and N_B), the pressure of the surrounding liquid p_l^* as calculated from the virial is given. Δp^* is the difference of pressure between the bubble and the surrounding liquid. The pressure inside the bubble was estimated from the thermodynamic route, i.e. by finding the pressure and composition for which the chemical potentials of the two components are the same in the liquid and vapour phases. ρ_l^* and ρ_v^* are the overall densities of the liquid and the bubble and $x_{A,v}$ is the composition of the vapour, as obtained from the radial overall and partial density profiles. The composition of the liquid $x_{A,l}$ remains very close to 0.75, with maximum deviations of 0.003 from this value.

Besides the radial density profile, we also calculated the radial concentration profile dividing the density of particles of type A by the total density for each radial distance. A sample profile is shown in Fig. 9.2 (b). The concentration of particles of type A is higher in the liquid than in the vapour phase, similarly to what was observed in the direct coexistence simulations. As in this case the volume of the gas phase is relatively small, the composition of the liquid phase remains fairly close to the starting composition, namely, $x_{A,l} \simeq 0.75$. However, the molar fraction of A in the vapour phase is again slightly lower than that in the surrounding liquid ($x_{A,v} \approx 0.66$). As explained before, this is due to the fact that the strength of the crossed interactions is a 10 % lower than that of like-interactions. In general in all the *NVT* seeding simulations performed in this work, the concentrations of

the bubbles are within $x_{a,v} \approx 0.670$ - 0.673 and that of the surrounding liquid is typically within $x_{A,l} \approx 0.750$ - 0.753 .

Alternatively, one can also resort to the equimolar Gibbs dividing surface as a criterion to define the bubble radius [66, 9]. The Gibbs dividing surface is obtained by assuming that the density of the liquid and the gas phases are constant up to the dividing surface with radius, R_G . In multi-component systems, a Gibbs dividing surface can be defined for each component. Here we defined the Gibbs radius using the majority component A:

$$N_A = V_{bubble}\rho_{A,v} + (V - V_{bubble})\rho_{A,l} \quad (9.12)$$

where V_{bubble} and V are, respectively, the volume of the bubble and of the simulation box. Substituting the volume of the bubble by:

$$V_{bubble} = \frac{4}{3}\pi R_G^3 \quad (9.13)$$

and reorganising we obtain that the Gibbs radius can be estimated as:

$$R_G = \left(\frac{3}{4\pi} \frac{N_A - L^3\rho_{A,l}}{\rho_{A,v} - \rho_{A,l}} \right)^{1/3} \quad (9.14)$$

where L is the edge of the simulation box. As mentioned before, we could have also defined the Gibbs radii using the minority component, B. These two Gibbs radii are only identical when the composition in the liquid and vapor phases are the same. As can be seen in Tables I and III, in our system this is neither true at coexistence nor at states where nucleation is studied. As discussed before, as a consequence of the reduced crossed interactions the minority component tends to go to the vapor phase, where interactions are less relevant. From Eq. 9.12, it is easy to see that this leads to $R_{G,B} > R_{G,A}$. However, as can be seen in Table 9.6, this effect is mild in our system. $R_{G,B}$ is only about 2 % bigger than $R_{G,A}$. Consequently, nucleation rates calculated with $R_{G,B}$ are 0-6 orders of magnitude smaller than those calculated with $R_{G,A}$, but, as will be shown later, this difference is within the uncertainty of our calculations. Since it seems more sensible to use the majority component, we have chosen to use $R_{G,A}$ in our calculations. In what follows, for simplicity in the notation, this radius will be denoted R_G .

As can be seen in Fig. 9.3(a) and Tables 9.4 and 9.5, the Gibbs radius is systematically larger than the equidensity radius. Taking into account Eqs. 9.2 and 9.5, this means that the Gibbs radius will lead to a higher cavitation free energy barrier and, consequently, to a lower cavitation rate than the equidensity radius. The same trend was also observed in previous Seeding studies of cavitation [9, 10, 11] (see Fig. 9.3(a)) and droplet nucleation [11] in the pure TSF-LJ system. Gibbs radii are not provided in Refs. [10, 11], but they can be estimated from the data reported in Ref. [11]. The results for the pure TSF-LJ system using the Gibbs radii are also included in Figs. 9.3 and 9.5.

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

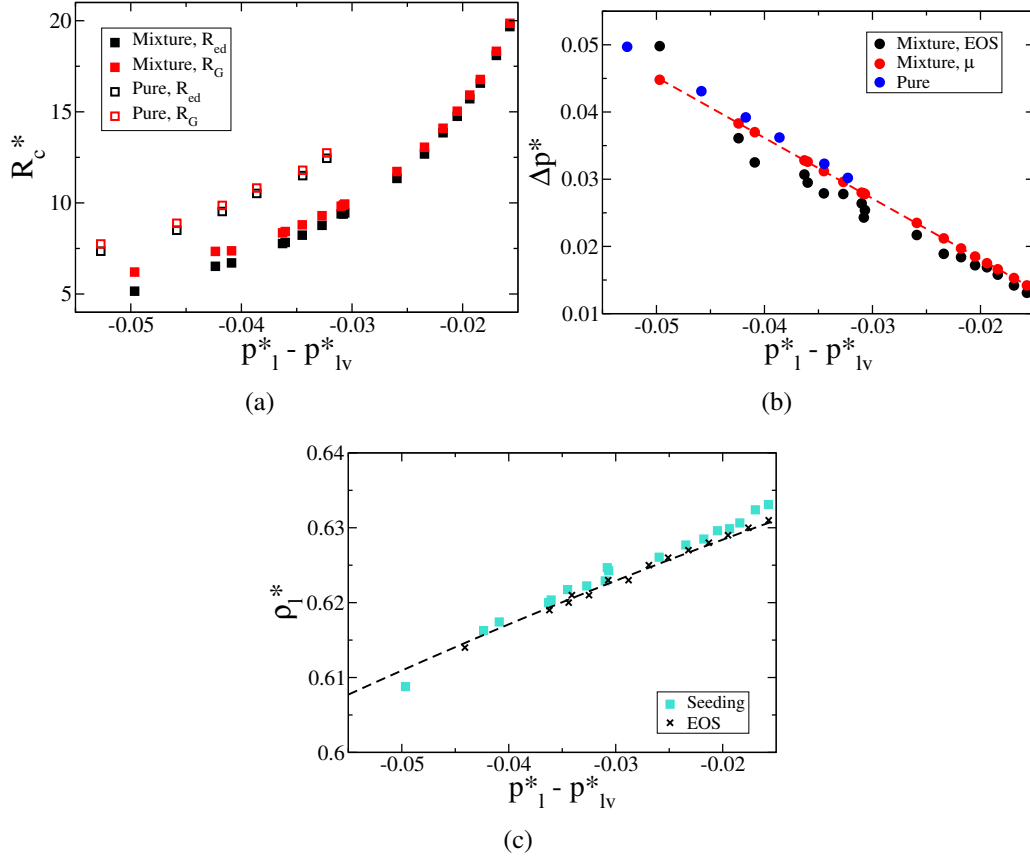


Figure 9.3. (a) Radius of the critical bubble as a function of the stretching pressure (measured as $p_l^* - p_{lv}^*$, with $p_{lv}^* = 0,0341(3)$). Solid black squares were obtained in this work with the equidensity criterion and solid red squares with the Gibbs criterion. Open symbols show the radii of bubbles for the pure TSF-LJ system reported in literature [11, 10] (the Gibbs radii were calculated in this work with the data provided in those references). (b) Bubble-liquid pressure difference as a function of $p_l^* - p_{lv}^*$. Black dots were obtained by measuring the density inside the bubble and using an EOS to get the pressure of the bubble, whereas red dots were obtained by looking for the conditions at which the chemical potentials of components A and B in the bubble and surrounding liquid are equal. For comparison, data from the literature of the pressure difference between the bubble and the surrounding liquid for the pure TSF-LJ are also shown with blue symbols (calculated by imposing that the chemical potential in the bubble and surrounding liquid is equal) [11, 10]. Δp^* shows a fairly linear behaviour, and is fitted to $\Delta p^* = 4,1787 \cdot 10^{-5} - 0,90275 (p_l^* - p_{lv}^*)$. (c) Density of the surrounding liquid, ρ_l^* , as a function of $p_l^* - p_{lv}^*$. Black crosses were obtained by performing *NpT* simulations of a liquid with $x_{A,l} = 0,75$. This EOS was fitted to a second degree polynomial ($\rho_l^* = 0,63835 + 0,46246 (p_l^* - p_{lv}^*) - 1,7164 (p_l^* - p_{lv}^*)^2$). For comparison, light blue symbols show the density of the liquid resulting from the fit of the radial density profile to a sigmoid function versus the virial pressure in the Seeding simulations.

Following previous work on one-component systems, [10, 11, 28] we checked what happens to the stabilised bubbles in the NVT ensemble when simulated in the NpT ensemble. For that aim, we launched 36 simulations in the NpT ensemble starting from bubble-liquid configurations taken along the trajectory of system with index 9 in Table 9.3 at the corresponding p_l^* ($p_l^* = 0,0031$). The outcome of those simulations is shown in Fig. 9.4, where the evolution of the total density of the system in all the NpT simulations is monitored. As can be seen, in about half of the trajectories the bubble dissolves and in the other half the bubble grows irreversibly to the vapour phase, indicating that the cluster is indeed critical.

One might intuitively expect that by virtue of the Gibbs phase rule, for binary systems it would be possible to have a critical cluster in stable equilibrium at constant p and T . Indeed, this has been exploited to have a planar interface of a binary system at equilibrium in the NpT ensemble [68, 69], but also to stabilize spherical crystal seeds of NaCl [68] in coexistence with a salt solution and of methane hydrate in coexistence with water with some methane dissolved [70]. However, as we have just seen, the critical bubbles in the binary symmetrical TSF-LJ mixture cannot be stabilised in the NpT ensemble. So, why is possible to stabilise the critical seed in the NpT ensemble for some multi-component systems but not for others? Further work is needed to clarify this issue, but it is important to highlight that in all cases in which stable clusters in the NpT ensemble were achieved, they had constant composition, given by the stoichiometry of the crystals (the NaCl rock salt and the methane hydrate), whereas in our case, the composition of the bubbles is not fixed. Small fluctuations in the composition of the clusters change the free energy barrier for bubble formation, making the cluster precritical or postcritical at the specified p and T and therefore, leading to their dissolution or growth. As for the one-component systems, we found that the bubbles only remain stable in simulations at constant volume.

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

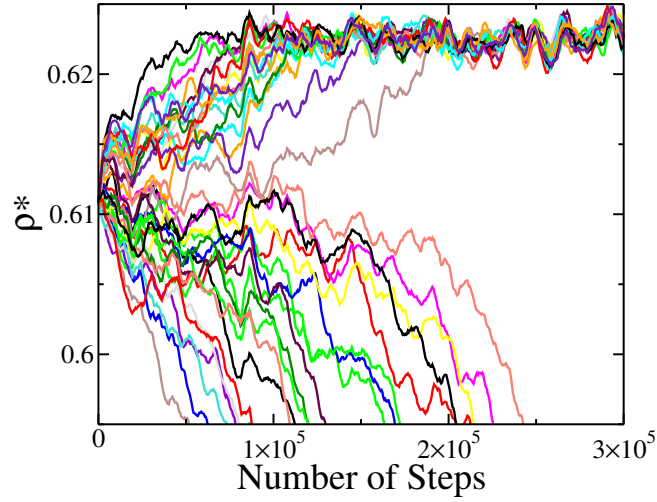


Figure 9.4. Evolution of the density of the system with time for 36 *NpT* simulations starting from different configurations collected along the *NVT* trajectory of bubble-liquid system with index 9 in Table 9.3. As can be seen, in about half of the trajectories the bubble dissolves and in the other half it leads to the vapour phase.

Pressure difference between the bubble and the surrounding liquid, Δp^*

Once we have estimated the bubble size, we proceed to calculate the difference of pressure between the bubble and the surrounding liquid, $\Delta p^* = p_{bubble}^* - p_l^*$, which is the other quantity needed to estimate ΔG_c (Eq. 9.5). In this work, we followed two different routes for this aim. In both approaches the pressure of the liquid that surrounds the bubble, p_l^* , was taken as the virial pressure in the *NVT* simulations, as provided by GROMACS [43]. Note that as we are dealing with an heterogeneous system, in which the bubble is in coexistence with the liquid, the pressure is not uniform in the system. But the average of the pressure tensor in the whole system coincides with that of the external phase, i.e., with that of the liquid [71]. The pressure of the liquid in all the Seeding simulations is reported in Table 9.3. The difference between the two methods relies on how to estimate the pressure inside the bubble, p_{bubble}^* .

In the first approach, the pressure inside the bubble is taken as the mechanical pressure, which can be estimated from the density and composition inside the bubble together with an EOS for the bulk vapour phase obtained from simulations ($p_{bubble}^* = p^*(\rho_v^*, x_{A,v})$). We checked that the EOS of the bulk vapour shows a mild dependence with composition within the range $x_{A,v}=0.670$ - 0.673 . This is rather convenient, because even though the composition of the bubbles is not exactly the same in all the Seeding simulations, it remains within these boundaries and the use of same bulk EOS for all the bubbles is justified. Here, the EOS was calculated by performing *NpT* MD simulations of a vapour with composition $x_{A,v} = 0,672$ and sweeping pressures within $p^* = 0.002$ - 0.033 .

In the second approach we use the thermodynamic route to estimate p_{bubble}^* . The equilibrium established between the bubble and the surrounding liquid im-

plies that the chemical potential of each component is the same in the two phases. The pressure inside the bubble is the one that fulfils this condition, which can be obtained from the chemical potentials calculated in Section 9.4.1 and shown in Fig. 9.1(a). The procedure is as follows. First, we estimate the chemical potentials of components A and B in a liquid with $x_{A,l} = 0,75$ at pressure p_l^* , namely, $\mu_{A,l}(p_l^*, x_{A,l})$ and $\mu_{B,l}(p_l^*, x_{A,l})$. The grey vertical line in Fig. 9.1(a) marks the pressure of the surrounding liquid, p_l^* , for the system with index 10 (Table 9.3), and the two horizontal grey lines mark the chemical potentials of components A and B in such liquid. Second, we look for the crossing points of these horizontal lines with the chemical potential lines of the corresponding component in the vapour phase at several vapour compositions ($x_{A,v} = 0,60, 0,65$ and $0,70$). At these crossing points the chemical potential of each component is the same in the liquid and in the vapour at concentration $x_{A,v}$, i.e. they fulfil $\mu_{A,l}(p_l^*, x_{A,l}) = \mu_{A,v}(p_v^*, x_{A,v})$ (purple symbols) and $\mu_{B,l}(p_l^*, x_{A,l}) = \mu_{B,v}(p_v^*, x_{A,v})$ (red symbols). These crossing points are represented and fitted to straight lines in Fig. 9.1(c). Only at the crossing point between these two lines, the equality of chemical potentials of the two components in both phases occurs at the same composition of the vapour phase, $x_{A,v}$, and at the same vapour pressure p_v^* , giving the equilibrium pressure inside the bubble p_{bubble}^* and its composition. For the system labelled with index 10 and shown in Fig. 9.1 (c), the pressure and composition of the bubble in equilibrium with the liquid are: $p_{bubble}^* = 0,0316$ and $x_{A,v} = 0,671$, which compare well with the values $p_{bubble}^* = 0,0309$ and $x_{A,v} = 0,656$ obtained with the first described method, i.e., using estimates of the density and composition inside the bubble together with the simulated EOS of the bulk vapour.

The results of Δp^* obtained from the mechanical and thermodynamic routes are plotted jointly in Fig. 9.3 (b) for comparison. As can be seen, both methods give results consistent with each other, but the chemical potential route provides less noisy data than the EOS route. Consistently with previous findings in the pure system, this means that the mechanical pressure is equivalent to the thermodynamic pressure [11, 72]. Note that this does not always hold, as has been shown in a recent study of hard-sphere crystal nucleation [28]. The higher statistical uncertainty in the mechanical pressure is expected, given the difficulty of accurately estimating the density inside the bubble. The number of vapour particles is very small and fluctuations in the number of particles lead to relatively large changes in the density. Besides, only the results obtained from the thermodynamic route guarantee that the chemical potentials are the same in the bubble and the surrounding liquid. For those reasons, the values of Δp^* obtained from the chemical potential route are the ones that will be used in the remaining of the article (these data are tabulated in Table 9.3). Curiously, as can be seen in Fig. 9.3(b), the difference of pressure between the bubble and surrounding liquid is very similar in the pure and the symmetrical binary TSF-LJ mixture, when compared at the same stretching $p_l^* - p_{lv}^*$, despite the bubbles being much bigger in the pure system.

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by *NVT* Seeding simulations

Index	R_{ed}^*	γ_{ed}^*	$\Delta G_{ed}/(k_B T)$	K_{ed}^*	$\log(J_{ed}^*)$	V_{bubble}/V_{box}
0	5.2	0.116	16.4	0.165	-8	0.04
1	6.5	0.125	28.3	0.174	-13	0.03
2	6.7	0.124	29.8	0.173	-14	0.03
3	7.8	0.128	41.1	0.177	-19	0.05
4	7.8	0.128	41.8	0.177	-19	0.05
5	8.2	0.128	46.4	0.178	-21	0.06
6	8.8	0.130	53.2	0.179	-24	0.07
7	9.4	0.131	61.6	0.180	-27	0.09
8	9.5	0.131	62.5	0.180	-28	0.09
9	9.4	0.134	63.1	0.182	-28	0.02
10	11.3	0.133	91.4	0.182	-40	0.03
11	12.7	0.135	115.5	0.184	-51	0.04
12	13.9	0.136	139.5	0.185	-61	0.06
13	14.8	0.137	158.7	0.186	-70	0.07
14	15.7	0.137	181.2	0.186	-79	0.08
15	16.6	0.138	201.9	0.187	-88	0.10
16	18.1	0.138	241.6	0.188	-106	0.13
17	19.7	0.139	288.1	0.189	-126	0.16

Table 9.4. Cavitation rates, J_{ed}^* , obtained with Seeding using the equidensity criterion to estimate the critical radii, along with the interfacial free energy γ_{ed}^* , free energy barrier, $\Delta G_{ed}/(k_B T)$, and kinetic factor, K_{ed}^* . The fraction of system volume occupied by the bubble, V_{bubble}/V_{box} , is also given.

Index	R_G^*	γ_G^*	$\Delta G_G/(k_B T)$	K_G^*	$\log(J_G^*)$
0	6.2	0.139	28.8	0.181	-13
1	7.3	0.140	39.0	0.183	-18
2	7.4	0.136	45.5	0.186	-21
3	8.4	0.137	53.4	0.185	-24
4	8.4	0.137	54.1	0.185	-24
5	8.8	0.137	60.2	0.186	-27
6	9.3	0.138	65.1	0.185	-29
7	9.9	0.138	76.3	0.187	-34
8	9.9	0.138	75.9	0.186	-34
9	9.8	0.140	69.9	0.185	-31
10	11.7	0.138	102.1	0.186	-45
11	13.1	0.138	126.3	0.186	-56
12	14.1	0.139	152.2	0.188	-67
13	15.0	0.139	177.1	0.189	-78
14	15.9	0.139	198.5	0.189	-87
15	16.8	0.139	219.6	0.189	-96
16	18.3	0.140	264.9	0.191	-116
17	19.9	0.141	309.7	0.191	-135

Tabla 9.5. Cavitation rates, J_G^* , obtained with Seeding using the Gibbs criterion to estimate the critical radii, along with the interfacial free energy γ_G^* , free energy barrier, $\Delta G_G/(k_B T)$, and kinetic factor, K_G^* .

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by NVT Seeding simulations

Index	$R_{G,A}^*$	$R_{G,B}^*$	$R_{G,AB}^*$	$\log(J_G^*)$	$\log(J_{G,B}^*)$	$\log(J_{G,AB}^*)$
0	6.21	6.22	6.21	-13	-13	-13
1	7.34	7.25	7.30	-18	-18	-18
2	7.37	7.73	7.55	-18	-21	-19
3	8.36	8.48	8.42	-23	-24	-23
4	8.43	8.54	8.48	-23	-24	-24
5	8.80	8.97	8.89	-25	-27	-26
6	9.30	9.38	9.34	-28	-29	-29
7	9.82	9.73	9.77	-32	-31	-32
8	9.94	10.08	10.01	-32	-34	-33
9	9.88	10.09	9.98	-32	-34	-33
10	11.72	11.77	11.75	-45	-45	-45
11	13.06	13.07	13.06	-55	-56	-55
12	14.10	14.26	14.18	-65	-67	-66
13	15.03	15.30	15.17	-74	-78	-76
14	15.92	16.20	16.06	-82	-87	-85
15	16.77	17.04	16.91	-92	-96	-94
16	18.32	18.66	18.49	-110	-116	-113
17	19.86	20.16	20.01	-129	-135	-132

Tabla 9.6. Gibbs radii calculated using component A ($R_{G,A}$), component B ($R_{G,B}$) and the average ($R_{G,AB}$), as well as the corresponding nucleation rates (J_G^*) obtained with these radii. In the remaining of the article $R_{G,A}$ is designed simply as R_G for simplicity in the notation.

Density of the metastable liquid, ρ_l^*

The density of the metastable liquid, ρ_l^* , needed to calculate the kinetic factor K , Eq. 9.7, is shown in Fig. 9.3(b). Again we tested two possible ways to estimate this density. In the first one, we used the EOS of the bulk liquid with $x_{A,l} = 0,75$ to obtain the density at the corresponding liquid pressure p_l^* , obtained from the virial pressure in Seeding simulations. In the second approach, the density is directly measured from the Seeding simulations, using the sigmoid fit. As can be seen in Fig. 9.3(c), the agreement between both sets of data is fairly good, except for the point at the lower pressure and some of the points at the highest pressures. It is also worth pointing out that the Seeding points that exhibit the larger departures from the EOS are precisely those with a higher V_{bubble}/V_{box} ratio (see Table 9.4), which might be indicative that these small deviations arise from finite size effects. In any case, differences are always lower than 0.3 %, which can be taken as an indication that finite size effects are not very significant in any of our Seeding simulations.

Due to the reduced cross interactions in the mixture, the liquid density is lower than in the pure system. Therefore, the kinetic factor K is about 15 % lower in the mixture [11] both because of the smaller bubble size and the reduced density

of the liquid, as compared to those of the pure system at the same stretching.

Cavitation free energy barrier and rate

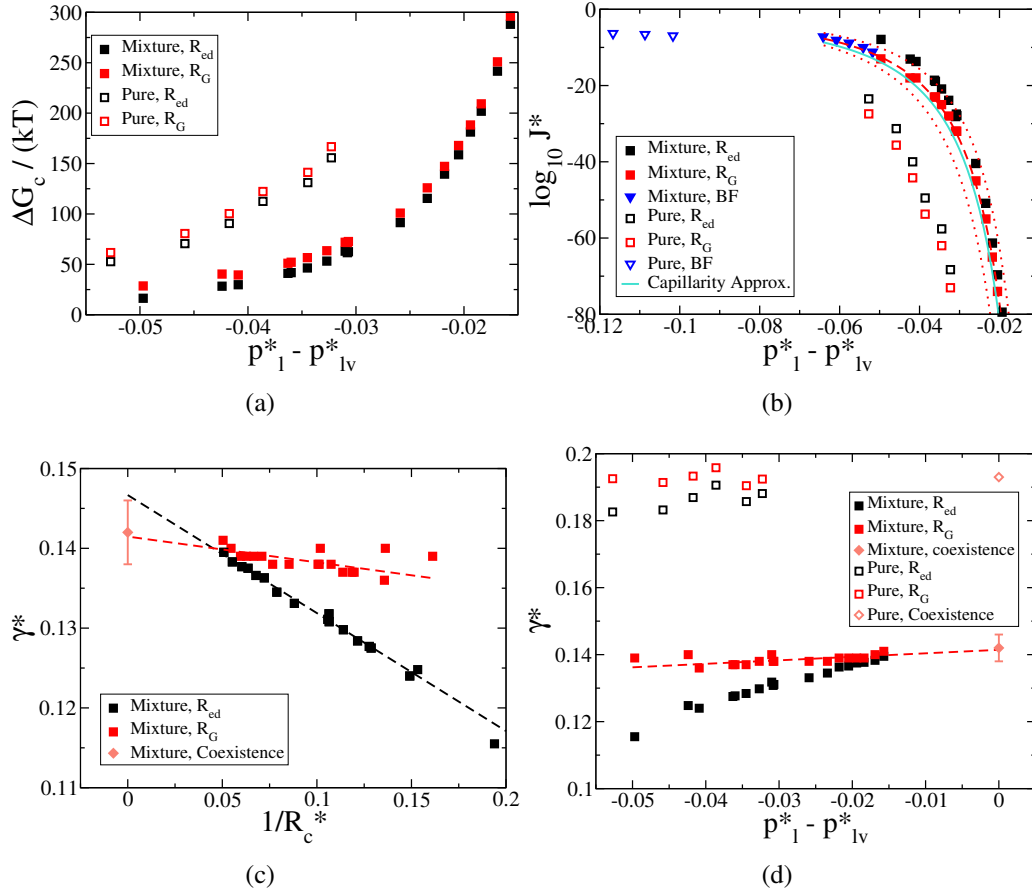


Figure 9.5. (a) Cavitation free energy barrier and (b) decimal logarithm of the cavitation rate as a function of $p_l^* - p_{lv}^*$. (c) Interfacial free energy as a function of the inverse of the radius of the critical bubble and (d) as a function of $p_l^* - p_{lv}^*$. In all panels, black squares show results obtained with the equidensity radius, and red squares with the Gibbs radius. Solid symbols show data for the mixture studied in this work, and open symbols display the results for the pure TSF-LJ system reported in Ref. [11]. Blue triangles in (b) show rates obtained from brute force simulations. In (c) and (d) the interfacial free energy at coexistence for the pure and mixture systems are represented with a pink diamond. In (d) γ^* was fitted to a straight line $\gamma^* = 0.14089 + 0.079549(p_l^* - p_{lv}^*)$, that is used to obtain the CNT-like fit shown by the red dot-dashed line in panel (b). The red dotted lines in panel (b) delimit the uncertainty in the rate.

Now that we have estimated the radius of the critical cluster (R_c), the difference of pressure inside and outside the bubble (Δp^*) and the density of the metastable liquid, we can proceed to calculate the free energy barrier for cavitation using

9. Estimation of bubble cavitation rates in a symmetrical Lennard-Jones mixture by NVT Seeding simulations

Eq. 9.5. The results as a function of stretching relative to the coexistence ($p_l^* - p_{lv}^*$) are shown in Fig. 9.5 (a). As the Gibbs radii are larger than the equidensity radii, the free energy barrier calculated with the Gibbs dividing surface is larger, the difference increasing with stretching as the critical bubble gets smaller. However, both sets of data support the conclusion that the free energy barrier is significantly lower in the mixture than in the pure TSF-LJ system, when compared at the same stretching relative to coexistence. Interestingly, a similar trend was observed in a simulation study on the effect of composition on the nucleation of droplets from a LJ binary mixture [18].

Next we present the cavitation rates obtained from Eq. 9.2 using the data summarised in Tables 9.4 and 9.5. As can be seen in Fig. 9.5(b), the small differences in the free energy barrier obtained with the two defined radii are also visible in the nucleation rates. Rates are lower using the Gibbs criteria. Both sets of data give consistent results with brute force simulations, although those derived from the Gibbs radii show a better agreement. However, this should be taken with care, because for the pure TSF-LJ system, R_G also coincides better with brute-force simulations [9], but at lower metastabilities R_{ed} provides rates consistent with Umbrella Sampling [11].

Interfacial free energy

The interfacial free energy can be obtained from Laplace equation (Eq. 9.4). The values calculated from the equidensity and Gibbs criteria are shown as a function of the inverse radius and as a function of $p_l^* - p_{lv}^*$ in Figs. 9.5(c) and (d), respectively. As can be seen, the extrapolation of both sets of data to infinite radius give coherent results with our calculation of the interfacial free energy at coexistence, but the values of γ obtained from R_G exhibit a considerably smaller slope than those derived from R_{ed} , in this latter case predicting that the cost of creating a bubble-liquid interface is rather insensitive to the curvature of the bubble, adopting values close to that of the planar interface from very small sizes.

The values of γ are compared with those of the pure TSF-LJ system [11] in Fig. 9.5 (d). For the pure TSF-LJ system γ was estimated using R_{ed} [11], because it gave rates coherent with those from Umbrella Sampling [9]. Consistently with the results in the thermodynamic limit, the interfacial free energy is systematically larger for the pure system than for the symmetrical mixture, with a slope intermediate between those derived from R_{ed} and R_G in the mixture. The lower interfacial free energy of the mixture as compared to that of the pure system explains why cavitation rates are significantly larger in the mixture.

9.4.4 Fit of the nucleation rate

The cavitation rate was fitted using CNT expressions as described in Ref. [10]. ΔG_c is a function of R_G and Δp (Eq. 9.5) and the kinetic factor K depends on R_G , Δp and ρ_l . As can be seen in Fig. 9.3, the dependence of Δp and ρ_l with

$p_l - p_{lv}$ follows a smooth behaviour, but that of R_G is more complex. Therefore, it is convenient to rewrite ΔG and A in terms of γ , which shows a nearly linear behaviour with $p_l - p_{lv}$ (Fig. 9.5 (d)). Using the fits of Δp , γ and ρ_l as a function of $p_l - p_{lv}$ provided in the captions to Figs. 9.3 and 9.5, we obtain J as a function of $p_l - p_{lv}$, which is plotted as a dashed red line Fig. 9.5 (b). The error in the rate comes from the uncertainty in the estimation of R_G , Δp and ρ_l , with the larger error coming from the critical radius. Assuming that the error in the critical radius is of about 0.3σ and neglecting the uncertainty in the other quantities, we can estimate the error in the rate, which is delimited by the red dotted lines in Fig. 9.5 (b). As can be seen, this fit and its error capture well the variation of the rates with the stretching. If instead of using the fit of γ we use the capillarity approximation (i.e., we assume that adopts the same value as the planar interface), the rate is very similar to that obtained using the rates calculated from R_G , which is expected as we have seen that γ was rather insensitive to the bubble curvature. Differences are much larger for the data derived from R_{ed} , because γ exhibits a larger dependence with curvature.

9.4.5 Cavitation free energy barrier as a function of metastability

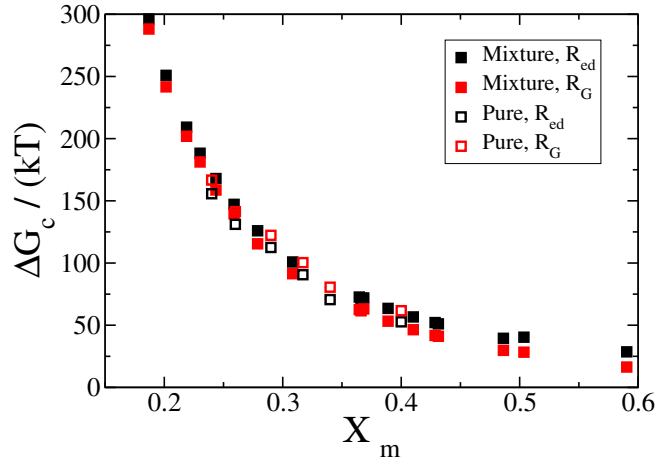


Figure 9.6. Cavitation free energy barrier for the TSF-LJ symmetrical mixture with $x_{A,l} = 0,75$ as a function of the scaled metastability. Free energy barriers obtained with the equidensity radius (R_{ed}) are shown as black squares and those obtained with the Gibbs radius (R_G) are shown as red squares. Solid symbols show the results obtained for the mixture studied in this work, and open symbols show the results for the pure TSF-LJ system at the same temperature ($T^* = 0,785$) taken from Ref. [11].

A theoretical work [73] has shown that in the pure LJ system the nucleation free energy barrier for the formation of bubbles is the same for all temperatures if

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compared at the same scaled metastability, defined as:

$$X_m = \frac{\mu_{nucl} - \mu_{coex}}{\mu_{spin} - \mu_{coex}} \quad (9.15)$$

where μ_{nucl} , μ_{coex} and μ_{spin} are the chemical potential of the liquid at nucleation, at coexistence and at the spinodal. With this definition X_m varies between 0 at coexistence and 1 at the spinodal. Interestingly, in a subsequent work [11], it was shown that the free energy barrier for droplet and bubble formation as a function of X_m also collapse into a single curve. In that regard, it seems that the free energy barrier for nucleation is the same for bubbles and droplets if compared at the same degree of scaled metastability.

In view of this, it is interesting to compare the free energy barrier for the LJ mixture as a function of X_m with that of the pure system. For a two component system, the driving force for nucleation depends on the chemical potential of the two components. Thus we define:

$$\mu = x_A \mu_A + x_B \mu_B \quad (9.16)$$

and this is the quantity that will be evaluated at coexistence, at the nucleation conditions and at the mechanical spinodal to estimate X_m . For a pure component system the spinodal is unique and is defined by the condition $(\partial p / \partial \rho)_T = 0$. For a binary mixture one can define two spinodals, the mechanical one given by $(\partial p / \partial \rho)_{T,x} = 0$ and the diffusional one defined as $(\partial \mu / \partial x)_{p,T} = 0$ [74, 75]. The location of these two spinodals can be quite different [74]. Since for pure components we found a correlation between the free energy barrier and X_m via the mechanical definition of the spinodal we shall explore the possibility of a similar correlation for mixtures when also using the mechanical definition of the spinodal. We estimated its location using an approximate method, as that described in Ref. [11]. In particular, we performed brute force simulations as those described in Section 9.4.2 at decreasing pressures. The spinodal is located at the highest pressure at which cavitation occurs immediately at the beginning of the simulations, without an induction period. We estimate that the spinodal is located at $p^* \approx -0,05$. The free energy barriers for bubble formation obtained either with R_{ed} and R_G are plotted as a function of X_m in Fig. 9.6, together with the results for the pure TSF-LJ system taken from previous work [11]. As can be seen, the free energy barrier for the pure and the binary systems adopt quite similar values when compared at the same scaled metastability. This means that the cost of creating a critical bubble does not depend much on the interactions (at least for symmetrical mixtures with low deviations of the reduced crossed interactions from unity as the ones considered) and it is mostly determined by the scaled metastability.

9.5 Conclusions

In this work, we have applied *NVT* Seeding to calculate bubble nucleation rates in a partially miscible binary symmetrical TSF-LJ mixture. The study was con-

ducted at a temperature that falls within the mixing region of the system and for which there are previous available data for the pure TSF-LJ model. One aspect that requires special care when implementing Seeding is the choice of an appropriate criterion to determine the bubble size. Here, we used both the equidensity radius and the equimolar (or Gibbs dividing surface) radius. Consistently with previous work [9, 11], the equidensity radii are systematically smaller than the Gibbs radii, leading to a lower free energy barrier and a higher nucleation rate. But what is the correct value of the critical bubble size? As mentioned before, the correct radius is the one corresponding to the surface of tension, and it is the one that enters in CNT expressions. Thus, we compared the nucleation rates derived from the equidensity and the Gibbs surface radii with those obtained from brute force simulations. Gibbs radii give rates closer to those obtained by brute force simulations. The same trend was found for bubble nucleation of water [13] and of the pure TSF-LJ, but at lower metastabilities, rates calculated with the equidensity radii are closer to those obtained by Forward-Flux sampling [9]. For droplet nucleation in the same system, equidensity nucleation rates are also in closer agreement with Umbrella Sampling results [11]. However, a recent study using enhancing sampling methods and Transition State Theory found results that are in agreement with Seeding, but obtained from Gibbs radii, and conclude that Forward-Flux sampling gives systematically higher rates [12, 7, 6]. Therefore, we can conclude that for the LJ model at high metastabilities, close to the region where brute force simulations are feasible, the Gibbs dividing surface radii give the correct nucleation rates. But at low metastabilities, where special simulation techniques are needed, the situation is not yet clear, as there are conflicting results using rigorous techniques [12]. Further work is needed to clarify why different methods provide different rates at low metastabilities.

In any case, the differences in the cavitation behaviour between the pure and symmetrical mixture are larger than differences between Seeding rates using different criteria for determining the bubble size. Therefore, conclusions about the difference in the cavitation behaviour in the two systems can be drawn. At the same stretching, measured as the pressure difference to coexistence, the critical bubble is smaller in the binary than in the pure system. The reason is that the interfacial free energy is about 25 % lower in the mixture than in the pure system, i.e., the free energy cost of creating a bubble is lower in the mixture. This is, at least in part, related to the fact that the critical temperature is lower in the mixture than in the pure system [40, 59]. Curiously, when comparing both systems at the same degree of scaled metastability, $X = (\mu_{liq} - \mu_{coex})/(\mu_{spin} - \mu_{coex})$ the free energy barrier is similar in both systems. This is an interesting result, as it was found in previous work that free energy barriers at different temperatures for bubble and droplet nucleation merged into a single curve when represented as a function of the scaled metastability [73, 11]. Our results suggest that this conclusion can also be extended to mixtures, at least for small deviations of the crossed interactions from those between like interactions, as the one considered here.

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In future work, it would be interesting to extend the *NVT* method to other systems and transitions, for example, to study droplet formation in strongly non ideal mixtures or crystallisation from a binary mixture. In principle, *NVT* should be applicable also in this case, however some difficulties might arise. For example, if important fractionation effects occur during nucleation (i.e. the composition of the nucleated and the parent phase are too different) is likely that to keep constant composition large simulation boxes are needed, or that other ensembles such as the semigrand canonical ensemble needs to be employed.

It would be also interesting to explore alternative routes to calculate the free energy cost of creating a bubble in the metastable liquid. A possibly viable method is to introduce an external potential that creates a bubble in the liquid and designing a reversible path that allows the calculation of the free energy by thermodynamic integration.

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Chapter 10

Conclusions

We have used Molecular Dynamics simulations to study phase transitions. Molecular simulations are a suitable tool to study crystal nucleation and cavitation of bubbles, because unlike experiments they have access to the relevant time and space scale, the nanoscale. Simulations provide detailed information at a molecular level. However, to study nucleation and cavitation, a detailed knowledge of the equilibrium phase diagram is required. We have used the Direct Coexistence method to obtain phase diagrams and coexistence points between phases. Once coexistence points are known, we studied nucleation of crystals and cavitation of bubbles in different liquid metastable systems. Nucleation and cavitation require overcoming an energy barrier, which can only be achieved through thermal fluctuations, making it a rare event. And the disparity between the lifetime of the critical nucleus and the occurrence of the event necessitates special rare event sampling methods that are often complicated and computationally expensive. As an alternative, the Seeding technique was proposed as an easy to use but approximate method. We implemented different versions of this technique. We studied systems like the water-NaCl one or other salty-water systems that are of great interest due to the abundance of saline aqueous solutions in various fields including atmospheric science, geology, and cryopreservation. We also studied pure water which has an unquestionable relevance and a Lennard-Jones mixture system. In the following, we enumerate the most important conclusions of this thesis.

We started by studying the liquid-solid equilibrium, by testing force fields for the simulation of aqueous solutions of ions:

- We calculated the complete phase diagram of the NaCl-H₂O, concluding that the ion-ion interactions of the JC-TIP4P/2005 model are too strong. The phase diagram obtained accurately predicts the coexistence between brine and ice, but the model underestimates the solubility of NaCl. It is worth noting that for the first time, the coexistence of hydrohalite-salt solution has been studied through simulation. The obtained results align with a linear extrapolation from experiments at high temperatures. However, at lower temperatures, it appears that the experimental curve will be underestimated. The coexistence could not be studied at the thermodynamic conditions (T, p)

10. Conclusions

where experiments were conducted due to the slow kinetics of the system. Two methods for applying the Direct Coexistence technique for mixture systems were proposed and compared – the Narrow Down method and the Equilibrium method. Both methods provide congruent results, although the first method is better to get a first estimate of coexistence, and the second one is more efficient if we know approximately where coexistence lies.

- We examined the freezing point depression of various salts, using the Madrid-2019 force field, which uses the TIP4P/2005 model for water and based on the pioneering idea of rescaling the charges of the ionic species to emulate charge transfer. It performs well in predicting the freezing point depression. However, a detailed analysis revealed that this was due to a cancellation of errors. Our studies of the coexistence conditions on salty water provide a good starting point for improving the simulation models and studying nucleation kinetics. Developing a model that predicts all coexistence curves and other thermodynamic and dynamic properties of aqueous salt solutions would be of great interest. The freezing point depression could become a standard property to consider when developing potentials for electrolytes, because it provides immediate information on the activity coefficient of electrolyte solutions along the coexistence curve. It should be taken into account that it is important to develop a model for electrolytes that reproduces the coexistence curve by subtracting the error introduced by the use of a water model that does not accurately reproduce water activity. Reproducing the freezing point depression without error cancellation would require a water model with correct temperature and enthalpy of fusion, as well as an ion force field capable of reproducing the osmotic coefficient up to high concentrations for temperatures well below the melting temperature of pure water.
- For the first time, Seeding has been successfully applied to a solute precipitation problem. This study paves the way for future simulation works on precipitation, which is a very important phenomenon. A judicious choice of the order parameter employed to identify the nucleus crystal has solved previously reported discrepancies of tens of orders of magnitude between the rate predicted by Seeding and that obtained by other rigorous techniques. By studying the precipitation of NaCl in saturated aqueous solutions, we confirmed the excessive tendency for ionic aggregation. The Seeding method combined with the Mislabelling criterion is a powerful approach for studying nucleation, even in complex media like ionic solutions.

Next, the liquid-vapor transition (cavitation), was addressed:

- Seeding was applied for the first time in the canonical ensemble to a system of great interest, such as water, specifically using the water TIP4P/2005 model. As well, for the first time, by obtaining the homogeneous cavitation line of water through simulation, which has allowed us to directly

compare with experimental results. The agreement with theory and experimental techniques, such as isobaric heating and isochoric cooling in quartz inclusions, for the study of cavitation is successful. However, the observed discrepancy with other techniques suggests that heterogeneous cavitation is occurring in those experiments. In our simulations, we used two different criteria for bubble radius identification: equidensity radii and Gibbs radii. We found that the equidensity radii consistently yielded smaller bubble sizes, lower free energy barriers, and higher cavitation rates compared to the Gibbs radii. It seems that the equidensity criterion is more appropriate for describing water cavitation because it extrapolates better to the spontaneous cavitation region.

- The Seeding NVT technique was successfully adapted to binary mixtures with a simple Lennard-Jones system. This is the first time this technique has been applied and adapted for a binary mixture system. We used a binary mixture of partially miscible Lennard-Jones liquids. We found that the interfacial free energy in the mixture is lower than in the equivalent pure system. As a result, the critical bubble size in the mixture is smaller. Additionally, we observed that the energetic cost of bubble formation is similar in both the pure and binary systems, if the liquid metastability is similar. Regarding the different criteria for bubble radius identification, the situation is more complex than for the water system. At high metastability, the radii of Gibbs provide more consistent nucleation rates. However, for low metastability where rare event simulation techniques are needed, the results are conflicting, and further investigation is required.

To sum up, it is possible to describe the phase diagram of the NaCl-water binary system, although new potentials are still needed to improve predictions. It has also been demonstrated that the Madrid-2019 model describes the freezing point depression well. The Seeding technique used with the Mislabelling criteria or the right bubble radius description provides good results for studying nucleation in complex systems not considered before, such as Lennard-Jones mixtures, water cavitation, and precipitation of NaCl in a supersaturated solution.